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In this issue of the Proceedings, we are publishing the papers presented at the Symposium on the Geology and Mineralogy of Atomic Mineral Deposits and Their Development for Use in the Nuclear Power Programme in India, held in New Delhi on 14–16 October 1968, under the auspices of INSA, Convener Prof. D. N. Wadia. The usual procedure followed in accepting papers is on the basis of the recommendations of the referee.

PROSPECTS OF UTILIZING INDIAN PHOSPHORITES AS A SOURCE OF URANIUM

by K. K. DAR, *Director, Atomic Minerals Division,*
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Uranium has already been extracted on a commercial scale from phosphatic rocks in the U.S.A. as far back as 1952 by the Blockson Chemical Company in Joliet, Illinois, in 1955 by the International Minerals and Chemical Corporation, Bartow, Florida, and in 1957 by the Tennessee Corporation. On the basis of the estimate that the United States is losing 1,200 tons U_3O_8 annually from this source and is likely to lose as much as 2,000 tons U_3O_8 per year in the manufacture of high-grade triple superphosphates, wet process phosphoric acid, ammonium phosphate and other technical grade phosphorus chemicals, the prospects of extracting uranium from the phosphatic deposits in India during the manufacture of superphosphates, etc., are examined. The uranium content of some of the Indian phosphatic rocks compares well with that in deposits in the U.S.A. and other countries. The problem of uranium extraction is discussed with respect to the feasibility of the chemical precipitation and solvent extraction methods. Investigation of phosphatic deposits in India is now in its incipient stages. It is, however, roughly estimated that with an average grade of 0·015 per cent U_3O_8 in phosphatic rocks, a 5-foot thick bed of phosphatic rock in a 1-mile square area would contain around 1,045 tons U_3O_8 of which 60 to 70 per cent would appear to be recoverable. These facts impart importance to phosphatic rocks as a large source of uranium. Certain lines of investigations necessary in this direction have also been suggested.

In another paper presented at this symposium, I have drawn attention to the large reserves of low-grade uranium resources in many shales, lignites and phosphorites, the utilization of which in the not too distant future is now being seriously considered. Of these, it seems, phosphorites are likely to be the first to be utilized for uranium extraction because, in the first place, large deposits thereof occur in many countries and, in the second, some experience on uranium extraction from them is already available. I propose to deal with this subject in the present paper.

Until a few years ago, the only phosphorite deposits known in India were those of Tiruchirapalli, South Arcot, Pondicherry and Mussoorie. With the priority that phosphorite exploration has recently received because of the domestic demand for fertilizers, many new deposits have been discovered and more are likely to be brought to light with continued exploration. The promising areas lie in Jammu and Kashmir; Chamba, Mandi, Bilaspur, Mahasu and Sirmur in Himachal Pradesh; Garhwal, Naini Tal, Pithoragarh and the Vindhyan tract in the plains in Uttar Pradesh; Udaipur and Jaisalmer and possibly also portions of Jodhpur in Rajasthan; Khammam, Warangal, Karimnagar, Adilabad, Cuddapah, Kurnool, Anantapur and Mehboobnagar in Andhra Pradesh; and the Laccadive islands. In some of these areas phosphate deposits have already been found.

The extraction of uranium from phosphorites is closely linked with the manufacture of wet-process phosphoric acid, ammonium phosphate, high-grade triple superphosphate, and other high-grade phosphorus chemicals as it can be recovered in an intermediary stage during their manufacture. With direct application of the phosphate rock to soil, with or without wetting with sulphuric acid, recovery of uranium is not possible.

The advantage of utilizing phosphate rocks for uranium extraction lies in the fact that mining of the phosphate deposit will not be necessary for this purpose alone as this would be done in any case for the manufacture of the aforesaid phosphorus products.

Now that there is a concerted effort for expansion of the fertilizer industry in India, wet-process phosphoric acid and other products may also come to be manufactured with the development of the industry. It is, therefore, necessary to examine the possibility of uranium extraction from these rocks as well as the preliminary work needed in this direction. To this end some basic ideas are presented in this paper.

URANIUM IN PHOSPHORITES

Sedimentary phosphatic deposits have been formed in different geological periods, but have attained considerable development in the Cambrian, Permian, Jurassic, Cretaceous and Tertiary times. They may show either mio-geosynclinal or platform facies (Mckelvey *et al.* 1953).

Most of the phosphorites contain small amounts of uranium but some show significally high values. Although in many cases uranium may be found to increase with the phosphate in the rock, this is not always so because of leaching by surface and ground waters of uranium and/or phosphate. Waters from phosphorite mines in the phosphoria formation contain as much as 0·022 ppm U, whereas surface and ground waters carry only 0·001 ppm U or less (Mckelvey and Carswell 1956). There is a possibility of such waters being found in radioactive phosphorites in India.

Swanson (1960) has compared the P_2O_5 and U_3O_8 content of phosphatic rocks of Montana and has shown that even the high-grade phosphorites (more than 31 per cent P_2O_5) do not contain more than 0·012 per cent uranium.

The chief phosphate minerals are collophane, a cryptocrystalline carbonate fluorapatite, and its microcrystalline, fibrous variety, francolite. In some phosphate rocks, however, aluminium or calcium-aluminium phosphates (wavellite or crandallite) may be the main phosphate minerals. The latter characterize the leached zone deposits of Florida, Senegal and Nigeria.

Uranium is commonly associated with carbonate-fluorapatite deposits, but in certain cases its concentrations may be found in the leached zone type deposits. Even in these leached zones uranium concentration does not follow Al at all but correlates well with PO_4, F and Ca. Aluminium phosphorites (wavellite and turquoise) can be uraniferous (Davidson and Atkins 1953; Heinrich 1958) due to U^{+4} substituting Cu in turquoise and Ca in crandallite (Heinrich 1958).

Krauskopf (1955) has indicated the concentrations and enrichment factors of certain rare metals in phosphorites, the best ppm averages being those of Ba, Cr, Ni, Pb, RE, Sr, V and Zn. While most of these and some others (Cu, Mo, Nb, Ni, Pb, Sr) have maximum concentrations of 3,000 ppm, the maximum for Ba is 1,000 ppm, for RE 1,500 ppm, for Cr 10,000 ppm and for V 30,000 ppm.

According to Heinrich (1958), who has compiled an excellent account of uranium in phosphatic rocks in various countries, sometimes minute amounts of secondary uranium minerals have been noted in altered phosphorites, e.g. autunite in the leached zone of Florida deposits, tyuyamumite in the weathered phosphoria formation in Utah and carnotite in some of the French North African deposits.

A thin sandy clay bed between the Bone Valley and the Hawthorn formations contains 0·002 to 0·015 per cent U_3O_8. Crandallite and Millisite concentrates from Bone Valley formation material have up to 0·03 to 0·04 per cent U whereas pure wavellite contains only 0·002 to 0·004 per cent U (Altschuler *et al.* 1956).

Some shales devoid of phosphatic nodules in Oklahoma and Kansas contain uranium, but with the appearance of phosphatic nodules their uranium content rises (Mckelvey and Nelson 1950). Phosphatic nodules of eastern Kansas contain 0·017 per cent U_3O_8 and those of south-eastern Kansas average 0·015 per cent eU (Ryan 1956).

Alaskan phosphorites contain 0·024 per cent U, those of Brazil 0·013 per cent U_3O_8 and British phosphorites free from calcite 0·01 to 0·10 per cent U_3O_8 (Heinrich 1958).

Davidson and Atkins (1953) note 0·002 to 0·004 per cent eU_3O_8 in Belgian phosphate deposits; 0·004 to 0·007 per cent eU_3O_8 in French deposits; 0·001 to 0·007 per cent eU_3O_8 in those of Germany; and 0·002 per cent eU_3O_8 in the phosphate beds of Albala in Spain, in which torbernite occurs.

The phosphatic deposits of Morocco contain 0·012 to 0·014 per cent U_3O_8; those of Algeria, 0·011 to 0·014 per cent U_3O_8; of Tunisia, 0·0047 to 0·009 per cent U_3O_8; of Kosseir and Safaga in the Middle East, 0·07 to 0·010 and 0·009 to 0·012 per cent eU_3O_8, respectively; and those of Nigeria, 0·004 to 0·007 per cent eU_3O_8 in the collophane type and 0·006 to 0·011 per cent eU_3O_8 in the wavellite type deposits (Davidson and Atkins 1953).

Guntz and Arene (1953) report 400 g/ton uranium in the Senegal deposits. Carbonaceous phosphorites in the Karoo formation in Nyasaland are reported by Davidson (1966) to contain 0·73 per cent U_3O_8.

URANIUM IN INDIAN PHOSPHATE DEPOSITS

The data on Indian phosphorites is still very meagre, but with the commencement of investigations in recent years much useful information is gradually becoming available.

The Extra-Peninsular phosphatic deposits occur in Chamba and Sirmur in Himachal Pradesh and in Dehra Dun, Garhwal and Pithoragarh in Uttar Pradesh in the black chert and carbonaceous shale member of the Lower Tals and immediately above the Krol-Tal contact. In Sirmur and in Dehra Dun, this horizon is quite persistent over considerable distances. At places, it contains phosphatic nodules and, at others, phosphatic pellets. In certain localities the phosphatic material is granular. The P_2O_5 content of these phosphatic rocks ranges from 5 to 30 per cent. The recently discovered phosphate deposits in Udaipur district, Rajasthan, including that of Kanpur, presently under investigation are, presumably, of pre-Cambrian Age as it is associated with Aravalli rocks.

(*i*) *Chamba:*

The phosphatic deposit of Chamba extends in a band for some 12 miles and contains phosphatic nodules, which give the impression of being fossil casts of some species of Lima, which are well developed, range in size up to 3–4 in., and are embedded in a black shaly matrix. The rocks present a thoroughly pitted appearance where the casts have been removed by weathering. The findings of a field party of the Atomic Minerals Division, which carried out a reconnaissance survey in this area, are presented in another paper in this symposium. Nagaraja Rao (1968) has identified fluorapatite, carbonate apatite, dahllite, wavellite, francolite and vauxite in nodules from the Siul Valley by x-ray study. The phosphate content of core material of the nodules from Dhaneli and of their outer shell is 1·03 and 0·50 per cent, respectively, which is very low, as is also the case with a sample of black shale with nodules from Prehli Adhwar which has analysed 1·60 per cent P_2O_5. Uranium content determined fluorimetrically in these samples is of the order of 0·0003 to 0·0017 per cent U_3O_8. Detailed work in this area has yet to be done.

(*ii*) *Sirmur:*

Krol rocks form elongate outcrops in two inverted synclines enclosed between the Krol thrust below and the local Giri thrust above them. East of Dadahu these rocks are cut up by smaller thrusts and the syncline becomes wider and more open and in which the Tal formations succeed the Krols

(Auden 1934; Pascoe 1959). The phosphatic horizons occur in the Lower Tals and are closely associated in places with black shales. The main Krol-Tal sequence forms an ovoidal synclinal outcrop, extends for a distance of some 16 miles between Mashrur in the west and Kandon in the east, and is about 7·5 miles across at its widest part. A similar but smaller outcrop, 9 miles in length and about 5·5 miles in width, runs between Korga on the west and Tons river in the east. Radiometric assays of some preliminary black shale samples collected by a survey party of the Atomic Minerals Division, have shown 0·010 to 0·022 per cent eU_3O_8. Similar samples from the Korga-Sakandon area have chemically analysed 0·011 to 0·018 per cent U_3O_8.

(*iii*) *Dehra Dun:*

Further east, the Krol-Tal succession reappears in the Krol syncline of Mussoorie which runs for a distance of some 12 miles in a NW-SE direction and is about 6 to 7 miles wide. Some portions of the margins of this geosyncline are under investigation by the Geological Survey of India, who have been able to locate phosphorite horizons with the help of GM Counters.

The phosphatic horizons here are usually 9 to 15 feet thick, but at places they attain a thickness of some 40 to 45 feet. X-ray examination of samples from Loharigarh area indicate the presence of fluorapatite and carbonate apatite (Nagaraja Rao 1968).

Some phosphorites and associated black shale samples from Loharigarh have analysed 0·022 to 0·114 per cent U_3O_8, *nil* ThO_2, and 6·31 to 33·41 per cent P_2O_5. Radiometric assays of similar samples from Masrana have reported 0·013 to 0·038 per cent eU_3O_8, from Loharigarh, 0·011 to 0·041 per cent eU_3O_8, from Kimoi, 0·025 and 0·029 per cent eU_3O_8; from Pari Tibba, 0·001 to 0·057 per cent eU_3O_8; and from Chamansari, 0·007 to 0·093 per cent eU_3O_8.

(*iv*) *Trichinopoly:*

Two samples from the 10-sq. mile occurrence of phosphatic nodules in the coastal Cretaceous deposits of Trichinopoly (Tiruchirapalli) extending between Nambakurichi and Varagupadi analysed, several years ago, 0·009 to 0·0095 per cent U_3O_8 (Dar 1964).

(*v*) *Pithoragarh and Udaipur:*

No information about the Pithoragarh and Udaipur occurrences is readily available but Nagaraja Rao (1968) reports dahllite in the Pithoragarh phosphatic rocks, and fluorapatite in the Udaipur phosphorite.

Such figures for uranium in Indian phosphate rocks as are now available compare favourably with those reported from other deposits in the world.

If uranium can be extracted from phosphorites in other countries, it stands to reason that this can be done in India as well.

URANIUM AVAILABLE IN INDIAN PHOSPHORITES

It would be profitable to assess as roughly as possible the likely amount of uranium that may be available in phosphorites in India. For this it would be appropriate to cite the example of Florida phosphate rocks from which recovery of uranium had been started by 1952 by the Blockson Chemical Company of Joliet, Illinois (Heinrich 1958), following research contracts which the U.S. Atomic Energy Commission entered into as early as the 1950s.

Florida land pebble phosphate contains 0·01 to 0·02 per cent U_3O_8. According to Kennedy (1966) the United States lost about 1,200 tons of U_3O_8 in 1955 in the wet-process phosphoric acid manufactured and will begin to lose as much as about 2,000 tons U_3O_8 per year, and that with the growth of the phosphate industry this loss of uranium would continue to grow at a progressively increasing rate. A similar situation will develop in India if steps are not taken in time to recover this important nuclear material.

It is easy to see that a 5-foot thick phosphorite bed with an average grade of 0·015 per cent U_3O_8 would contain over an area of 1 mile square some 1,045 tons U_3O_8, 60 to 70 per cent of which should be recoverable as we shall see presently. The uranium content of carbonaceous phosphorites, such as those of Loharigarh, is generally higher than in non-carbonaceous types and, consequently, the quantity of uranium available in them would be greater than in the latter.

EXTRACTION OF URANIUM FROM PHOSPHATE ROCKS

As far back as 1952, the Blockson Chemical Company employed chemical precipitation method by partial neutralization of wet-process phosphoric acid to form mono-sodium phosphate, after oxidation with a strong oxidizer, e.g. chlorine, which helped in retention of 80 to 90 per cent uranium in solution and precipitation of impurities consisting of Ca, Fe and Al. About 90 to 95 per cent uranium was then precipitated with sodium hydrosulphite as a gelatinous uranous phosphate. Filtration of this precipitate was effected with a diatomaceous earth filter aid and uranium in the product upgraded to 40 to 60 per cent U_3O_8 representing an over-all recovery of 60 to 70 per cent (Kennedy 1966). Calcination of the phosphate rock to eliminate organic impurities, not permissible in the technical grade phosphate chemicals produced by the Company, reduced uranium dissolution by 10 to 20 per cent (Stoltz 1958) and it is not known whether uranium recovery would have been effected had this rock not been calcined.

The International Minerals and Chemical Corporation employed in 1955 a solvent extraction process in which uranium was extracted from in-process phosphoric acid without neutralizing the acid to minimize interference in triple superphosphate manufacture. Both anionic and cationic resins were unsuccessful because of saturation loadings of 0·1 to 0·2 g/lit of resin. Solvents offered the greatest difficulty because of their insufficient stability, the most favourable being the alkyl pyrophosphate esters. Another difficulty was encountered in the reduction pits due to rapid formation of coatings of iron phosphate and gypsum on scrap iron which passivated the reaction. This was overcome by using a rotary stainless steel drum, the agitation in which prevented formation of coatings on iron. Only centrifuges proved satisfactory for separating organic from aqueous phases. The problem of stabilization of emulsions by continuous collection of fine solid particles in acid, mainly gypsum, at the organic-aqueous interface was substantially overcome by allowing the acid to stand for a few days before solvent extraction. Uranium load in the solvent was removed in a single stripping stage with 12 per cent solution of HF or a mixture of 12 per cent HF and 25 per cent H_2SO_4. The crude uranium tetrafluoride after drying contained 40 to 60 per cent U_3O_8 and it was necessary to refine by developing a satisfactory commercial procedure for it (Kennedy 1966). The Tennessee Corporation in 1957 also employed solvent extraction for uranium recovery.

Zefirov (1966) notes that it is important to develop suitable physically more stable solvents with high selectivity for extraction of various valuable constituents associated with uranium.

Lines of Investigations Necessary

A review of the foregoing facts shows that while, broadly speaking, prospects of uranium extraction from phosphate rocks presents a promising outlook, a good deal of fundamental work will still be required both in the field and in the laboratory.

This programme of investigations should include systematic mapping of the phosphorite horizons; demarcation of the boundaries of carbonaceous varieties of phosphorites and those which are not, as the former are likely to have a higher uranium content than the latter; marking of leached zones which are likely to be high in uranium; location of secondary uranium minerals which may, possibly, occur in some localities; systematic sampling; estimation of U_3O_8 or U in the phosphatic horizons; location of their stratigraphic positions and their correlation; study of P_2O_5/U_3O_8 ratios and possible uranium mobilization and its concentration at lower stratigraphic levels in favourable lithological horizons, or leaching of the phosphate leaving a uranium-rich rock behind.

The laboratory work should include identification of phosphate minerals present in the phosphorites in different areas; their relationship with uranium concentration, the differences in the concentrations of uranium in bioclastic and ovulitic phosphorites, physical beneficiation tests for various useful constituents of the phosphorites, and leaching tests for uranium using the neutralization and the solvent extraction and, possibly, other methods. Steps by appropriate agencies taken to develop physically stable solvents with high selectivity for recovery of different economic materials, associated with uranium in phosphatic rocks, would prove beneficial in meeting the extraction problems in the long run.

This investigation will require close collaboration and exchange of data and information between agencies concerned with and interested in different aspects of the problem to achieve the results aimed at.

Eventually, the by-product recovery of uranium and, maybe, of other useful minerals, will have to be correlated with the plans of the phosphate fertilizer industry and will thus depend, as stated earlier, on the products that are planned to be manufactured. The best interests of the country, it seems, will be served by a broad-based project embracing manufacture of wet-process phosphoric acid, ammonium phosphate, high-grade triple phosphate and technical quality phosphate chemicals; some of these are likely to find a market in neighbouring countries also. In this manner an effort can be made to prevent the loss of uranium which is otherwise likely to occur.

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PROGRESS IN HEAP-LEACHING INVESTIGATIONS ON DIFFERENT TYPES OF URANIUM ORES

by K. K. Dar, *Regional Director, Atomic Minerals Division,*
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On the consideration of the facts that uranium requirements in the 1981 to 2000 period will far exceed the existing reserves, and that future discoveries of high-grade surface and near-surface deposits are not likely to be as frequent as they were in the early days of uranium exploration, recourse to exploitation of small deposits of high-grade and large deposits of low-grade uranium would be inevitable. It is suggested that then heap-leaching of ores, the transportation cost of which would not be economic and for which the installation of conventional mills not warranted, will become necessary for uranium extraction.

The progress of work carried out on some domestic ores of different characteristics is reviewed in this paper. Attention has been drawn to the saving in time achieved with equivalent recoveries in comparison with time that is normally considered necessary for heap-leaching in countries where this method is being applied.

It is suggested that this method may also come to be employed for extraction of base metals from small and scattered domestic deposits which may otherwise remain unexploitable.

INTRODUCTION

Of late heap-leaching methods for extraction of uranium from small deposits of high-grade ores and other deposits of low-grade ores in out-of-the-way localities—in fact all ores the transportation cost of which to existing mills was likely to be uneconomic and for which the installation of a conventional plant not justified—have become the subject of much attention and investigation because of several reasons.

One important reason is that the world reserves (excluding those of the U.S.S.R., China, etc.) of high-grade uranium, estimated at 600,000 short tons on January 1, 1964, of which a sizeable amount has since been utilized, are expected to be depleted by 1980 with the rapid growth and expansion of nuclear power programmes, and the need for some 3,200,000 short tons of U_3O_8—which is six times the 1964 reserves—between the period 1981 and 2000 (Faulkner and McVey 1964).

The second is the realization that discoveries of large high-grade reserves are not likely to show the same frequency which marked the period 1950–1956 and that prospecting methods which were used in the 1945–1955 period are not likely to be so fruitful in the present period (Bowie 1964).

Consequently, it is apparent that the time is not far off when various nuclear countries of the world will have to draw upon small but high-grade ores as well as low-grade ores containing 0·005 to 0·03 per cent U_3O_8. Enormous reserves of such uranium exist in shales, lignites, phosphatic rocks, etc. —sources which were not generally considered exploitable hitherto—to meet future uranium requirements (Bowie 1964).

Notable amongst the countries which are trying the heap-leaching techniques are Argentine (Cechetto *et al.* 1964), Portugal (Andrade *et al.* 1964) and France. Japan (Anon. 1964) has utilized the pugging method.

The presently mined reserves in the U.S.A. and other countries are in the category of \$5 to \$10 per lb U_3O_8. But, by 1980, there will be need to work out ores in the \$10 to \$15 and \$15 to \$20 categories and, subsequently, perhaps even ores in the higher categories of more than \$20 per lb U_3O_8.

As ore characteristics and their mineralogical composition vary widely from place to place, each particular type of ore will require to be treated by a method most suitable for it. This now calls for research and development of processes for treatment of such ores by the time we come to exploit them.

Although it has been claimed that 35 per cent economy in cost of equpment, 20 per cent in acid consumption, 35 per cent in energy consumption and 50 to 100 per cent in transport cost is effected by employing heap-leaching (Cechetto *et al.* 1964), these figures would, naturally, be variable and depend on the nature and location of the deposits, cost of materials and ordinary technical skill locally available and similar other factors. On the whole, however, these methods appear to be most suitable for the type of deposits which are being considered here.

Presently, the high-grade ore reserves in India are small but large reserves of low-grade ores and ores below cut-off grade of 0·05 per cent U_3O_8 are available. These ores occur in phyllites, schists, quartzites and some granular rocks, etc., which are generally very different in character from the sandstone type uranium deposits of the U.S.A., France, etc. Because of their high transmissivity, enabling efficient acid attack on the contained uranium minerals, the sandstone type deposits do not require much grinding. The Indian uraniferous ores, on account of their hardness and imperfect permeability, or impervious character, introduce cost of grinding—a major cost in the operation—into the cost inventory. In order to reduce this cost, determination of maximum particle size commensurate with efficient leaching becomes an important parameter for study, in addition to other parameters such as consumption of acid and other reagents, control and maintenance of *p*H and Eh levels and of conditions necessary for preventing co-precipitation of associated elements in the cake.

The progress of investigations carried out in the Mineral Technology Laboratories of the Atomic Minerals Division of the Department of Atomic Energy on different types of ores from Umra and Udaisagar Prospects (Udaipur district, Rajasthan), Chhinjra-Dharmaor Prospect (Kulu district, Himachal Pradesh), Tunji Prospect (Chamoli district, Uttar Pradesh), Inderwa (Hazaribagh district, Bihar) and Neyveli Lignite Mine (South Arcot district, Madras) are reviewed and the problems encountered in the work discussed in this paper. The experimental data are summarized in Table I.

UMRA PROSPECT

The Umra uranium deposit (Dar and Nandi 1958; Dar 1964) is small. Uraninite with a host of secondary minerals, associated with pyrite and chalcopyrite and variable amounts of calcite, occurs along the sheared limestone/black shale contact. Secondary uranyl minerals predominate over primary uraninite. For leaching tests the ore was classified in three categories: (i) high grade (0·21 per cent U_3O_8 and above), (ii) medium grade (between 0·11 and 0·20 per cent U_3O_8) and (iii) low grade (0·10 per cent U_3O_8 and less). These were separately investigated. As medium- and low-grade ores contain more carbonate (10·6 per cent) than the high-grade ore (5·1 per cent), they were subjected to alkaline leaching.

High-grade ore—With 0·39 per cent U_3O_8 grade feed ground to −5 mesh (ASTM) size leached at a pulp density of 70 per cent with 63 lb/ton of 20·0 per cent H_2SO_4 at a pH of 2, leachability of 85 per cent in 24 hours was obtained without recirculation of the leach liquor. Crude cake precipitated with 35 lb/ton of commercial NaOH analysed 10 per cent U_3O_8. During this process 6 lb Cu per ton of ore treated was recovered by cementation.

Medium-grade ore—This −5 mesh (ASTM) size feed, assaying 0·12 per cent U_3O_8, indicated leachability of 78 per cent in 30 days with 20 lb/ton sodium carbonate at a pulp density of 50 per cent and pH of 10·2, without any recirculation of the leach liquor. The crude cake precipitated with 20 lb/ton NaOH analysed 50 per cent U_3O_8. Cementation tests carried out on this ore showed that 93 per cent of the uranium leached could be cemented with 13 lb/ton of iron.

Low-grade ore—Leachability of 86·6 per cent was obtained with a −5 mesh (ASTM) feed, analysing 0·05 per cent U_3O_8, on its treatment with 25 lb/ton Na_2CO_3 and 6 lb/ton $NaHCO_3$ at a pulp density of 60 per cent and pH of 10·2 in 20 days as first results of preliminary tests on this ore. The cake precipitated with 35 lb/ton commercial NaOH analysed 15·2 per cent U_3O_8.

UDAISAGAR PROSPECT

The Udaisagar ore is low grade and consists of crushed, weathered and partially kaolinized granitic material in which are embedded feldspar and phyllitic fragments. Uraninite associated with pyrite (3·2 per cent), both occurring as stringers and specks, as well as some secondary uranyl minerals (mainly autunite), constitute the ore. Some uranium occurs in a cationic state as a result of adsorption in clay (Jayaram 1968).

TABLE I

Table showing the summary of leaching work carried out on different samples received from different parts of India

Note: All experiments are conducted at room temperature

Sl. No.	Locality	Feed value % U_3O_8	Size of attack	H_2SO_4 used		Other reagents		Time of attack	Leach-ability %	Cake grade % U_3O_8
				Lb/ton	% Strength	Name	Lb/ton			
1	Udaisagar	0·03	30% + ¼″	6·5	0·166	–	–	5 hrs	70·0	6·0
2	Umra	(*a*) 0·39	– 5	63	20·0	–	–	24 hrs	85·0	10·0
		(*b*) 0·12	– 5	–	–	Na_2CO_3	20	30 days	78·0	50·0
		(*c*) 0·05	– 5	–	–	Na_2CO_3 $NaHCO_3$	25 6	20 days	86·6	10·2
3	Chhinjra	(*a*) 0·16	–10	54	3	MnO_2	10	32 days	63·0	3·0
		(*b*) 0·09	–10	50	3	MnO_2	10	28 days	65·1	–
		*(*c*) 0·06	–10	70	1	MnO_2	13	26 days	83·6	3·3
4	Tunji	0·20	– 5	27		MnO_2	4	1 day	64·0	6·4
5	Neyveli	(*a*) 0·018	– 5	36	2	nil	nil	28 days	36·0	–
		(*b*) 0·018	–20	97·2	1·1	nil	nil	3 days	50·0	–
		(*c*) 0·018	–20	97·2	1·1	NaCl	23·4	3 days	62·5	–
6	Inderwa	0·087	– ¼″	74·0	7·5	$KClO_3$	15·0	2 days	80·0	–

* Experimental test on a 10-ton sample.

Physical beneficiation on classified and unclassified material analysing 0·03 per cent U_3O_8 proved fruitless due to uniform distribution of uranium in fine sizes.

Agitation leaching, tried with 10 lb/ton of H_2SO_4 at 50 per cent pulp density, showed a leachability of 99 per cent in 20 hours, the low acid consumption being due in part to cationic state of uranium present and partly also to the hydrolysis of pyrite.

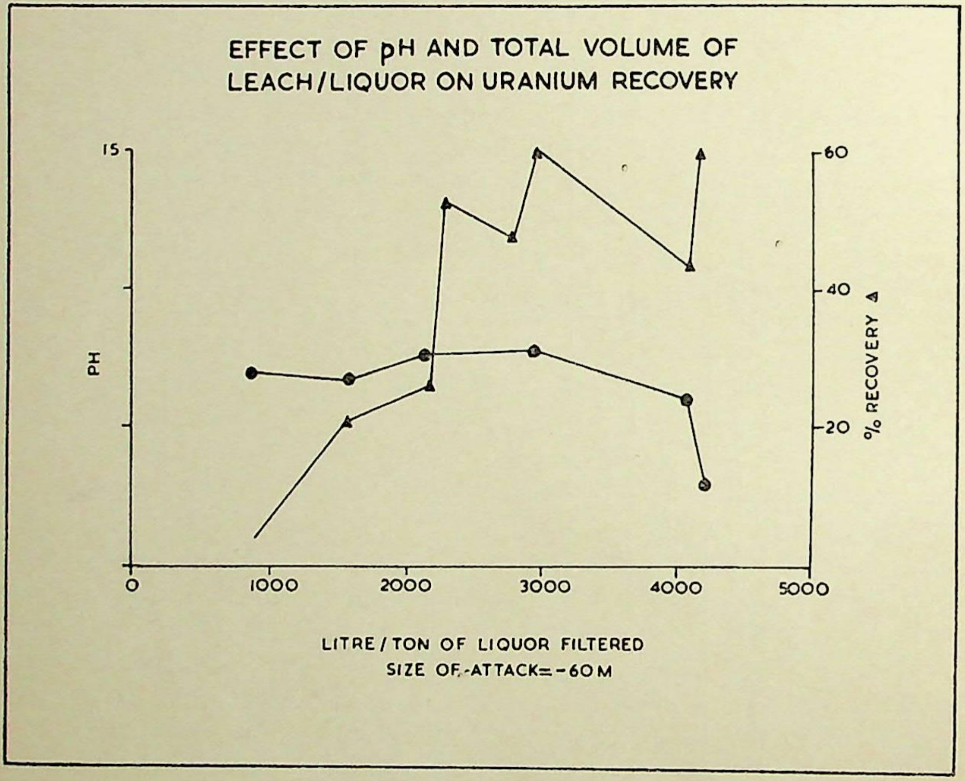

FIG. 1

These tests were followed by static leaching experiments, to save on cost of agitation, by varying the contact time, but keeping the pulp density constant at 62·5 per cent in all cases. It was found that the best leachability of 70 per cent was obtained with 6·5 lb/ton of 0·166 per cent H_2SO_4 in a 5-hr contact period, that any increase of attack time raised the pH of the leach liquor resulting in precipitation of uranium, and that finer grinding increased the specific surface of particles for attack and greater dissolution of Fe and Al resulting in the reduction of the cake grade. Undissolved cationic uranium in the residue, however, is recoverable by washing the residue with water, the recovery increasing with the quantity of water used (Jayaram 1968). The crude cake, precipitated with 15 lb/ton commercial NaOH, analysed only 4·5 per cent U_3O_8 at a recovery of 60 per cent (Fig. 1).

Chhinjra-Dharmaor Prospect

The ore is a compact, hard, fine-grained quartzite with some phyllitic material in which uranium occurs as veins, veinlets, interstitial fillings, smears and coatings of amorphous uraninite on quartz grains, and as replacement of quartz grains. Pyrite averages 1·5 per cent in the ore (Jayaram 1964).

Tabling was unsuccessful due to uniform distribution of uranium and its non-liberation up to a grind of −200 mesh. Anionic flotation of −200 mesh feed with oleic acid yielded concentrates with 78 per cent recovery, but cost of fine grinding would make flotation uneconomic in the Himalayas.

Likewise, agitation leaching of −200 mesh ore with 120 lb/ton H_2SO_4 at pulp density of 50 per cent, with 90 per cent recovery in the leach liquor, is uneconomic due to high acid consumption, high free acid left in the leach liquor and the fine grinding of the ore required.

Percolation leaching tests with 50 lb/ton of 3 per cent H_2SO_4 at 1·5 lit/hr/cm^2 and 10 lb/ton MnO_2 on −10 mesh (ASTM) feed analysing 0·09 per cent U_3O_8 showed that 65·1 per cent uranium was leachable in 28 days with 28 recirculations without any stage addition of acid.

In a second series of similar tests on −10 mesh feed analysing 0·16 per cent U_3O_8, at a percolation rate of 0·04 lit/hr/cm^2 with 54 lb/ton of 3 per cent H_2SO_4, and with 10 lb/ton MnO_2 mixed with the feed, leachability of 63 per cent was obtained in 32 days with daily recirculation of leach liquor. Cake obtained by precipitation with 35 lb/ton NaOH, however, analysed only 3·0 per cent U_3O_8.

In a test on 10 tons of 0·06 per cent U_3O_8 grade −10 mesh feed at the prospect site with 70 lb/ton 1 per cent H_2SO_4 and 13 lb/ton MnO_2 in 26 recirculations at percolation rate of 0·04 lit/hr/cm^2, 83·6 per cent uranium was leached but the cake obtained by using 40 lb/ton NaOH analysed only 3·3 per cent U_3O_8.

In both cases, the low value of uranium in the cake is due in part to dissolution of iron in the leach liquor and its co-precipitation with uranium in the cake and in part to peptization losses.

In all these percolation leaching tests, curing time of 17 hours was allowed between each leaching phase of 7 hours.

Tunji Prospect

Uraninite occurs as stringers, grains and smears in the cleavage planes of chlorite schist in which pyrite is seen as specks and stringers. The schist is also cut by thin granitic veins.

In a few preliminary static leaching tests carried out on −5 mesh feed analysing 0·20 per cent U_3O_8 with 27 lb/ton of H_2SO_4 and 4 lb/ton of MnO_2 at a pulp density of 77 per cent, 64·0 per cent of the uranium was leached. The cake obtained, however, analysed only 6·4 per cent U_3O_8.

NEYVELI LIGNITE MINE

Static leaching tests on the low-grade carbonaceous clay (0·018 per cent U_3O_8) samples with which 0·001 to 0·05 per cent Se, 0·01 to 0·25 per cent V, and trace amounts of Mo are associated (Dar 1964), a leachability of 36 per cent was obtained in 28 days with 36 lb/ton of 2 per cent H_2SO_4 at a pulp density of 28 per cent. The leach liquor was also found to contain 125 mg/lit of vanadium and some selenium. This work is still in progress.

Agitation leaching of this material with 97·2 lb/ton of 1·1 per cent H_2SO_4 and 23·4 lb/ton of NaCl raised the leachability to 62·5 per cent in three days. Without NaCl under the same conditions, only 50 per cent of the uranium was leached. It is, thus, seen that due to the existence of uranium in a cationic adsorbed state and of a reducing environment due to carbon and marcasite in the clay, the use of an exchanger is useful for effective recoveries.

INDERWA

The uraniferous amphibolite and migmatite sample from the Inderwa area contains significant amount of pyrite, chalcopyrite, covellite, malachite and calcite. Uraninite occurs as minute inclusions in hornblende.

Tabling tests on −60 mesh (ASTM) feed analysing 0·087 per cent U_3O_8 yielded a concentrate analysing 0·092 per cent U_3O_8 with a recovery of only 32·8 per cent. This is attributable to uniform distribution of uranium in all sized fractions. Clearly the ore is not amenable to such treatment. A rough test on this material ground to −200 mesh by hand panning showed a recovery of only 38·3 per cent in the concentrate analysing 0·24 per cent U_3O_8. Even with mechanical concentration of the material at −200 mesh, no significant increase in recovery may be expected as liberation is still incomplete at this size. For the same reason, flotation of the material would also not be fruitful.

Leaching of uranium from this ore also presents problems due to dissolution of high amounts of iron which passes into the cake, thereby lowering its grade. The presence of calcium carbonate increases acid consumption.

It was found in a series of tests on −5 mesh (ASTM) size feed of 0·087 per cent U_3O_8 grade that while with static leaching with 72 lb/ton of 10 per cent V/V H_2SO_4 and 15 lb/ton $KClO_3$ recovery of 77·8 per cent, respectively, was achieved, in percolation leaching with the same quantities and amounts of reagents, recovery was only 58·6 per cent. It would thus appear, subject to results of additional tests on other sizes of this material in hand, that with this ore higher leaching efficiency is likely to be obtained by static leaching than by percolation leaching.

$KClO_3$ is a more efficient oxidizer than MnO_2. Static leaching of −5 mesh feed with 72 lb/ton of 10 per cent V/V H_2SO_4 yielded recoveries of 77 per cent with 15 lb/ton of $KClO_3$ against 60 per cent with 15 lb/ton of MnO_2 (Fig. 2). None the less, it is necessary to find ways of increasing leachability with the use of cheaper MnO_2.

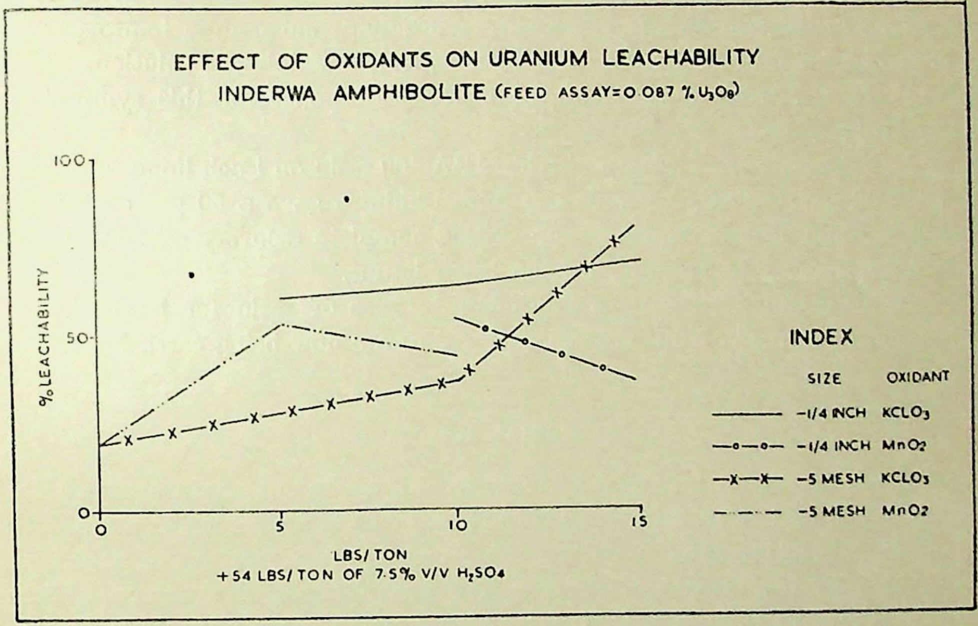

FIG. 2

PROBLEM OF PEPTIZATION

Leach liquors obtained in heap-leaching contain 300 to 900 mg/lit uranium but precipitation of sodium di-uranate with commercial NaOH leads to incomplete recovery in the cake because some of the uranium in solution complexes (i) with about 15 per cent carbonate present in the NaOH, (ii) with ferric hydroxide present in leach liquors as a positively charged suspensoid in a colloidal state thereby escaping precipitation, and (iii) complexing of $U(SO_4)_2 . 4H_2O$ in the leach liquors during precipitation with $Na_2SO_3 . 7H_2O$ and $Na_2SO_4 . 7H_2O$ formed on addition of NaOH to the leach liquor due to free sulphuric acid present, all these salts being water-soluble and therefore unable to precipitate.

Complexing of uranium with carbonate was reduced by careful maintenance of pH at 10·5 by controlling NaOH. Some data on this will be presented in another paper in this symposium.

Careful reduction of ferric oxide dissolved in the leach liquor to ferrous oxide by addition of scrap iron or zinc with resultant release of uranium which can be precipitated enabled increase in the cake value. With this loss of uranium due to peptization was reduced from 4·5 to 1·1 per cent.

The complexing of uranium sulphite with sodium sulphate and sulphite can be avoided by stripping uranium with resin and recirculation of the free acid, or recirculation of the barren liquor which contains free acid.

Complete reduction of all the ions in the leach liquor with scrap iron or zinc resulting in the cementation of uranium and copper improves the grade of uranium recovered in the cement, iron remaining in solution. This aspect of the work is the subject of another paper for this symposium (Dar 1970).

Experiments tried with amberlite IRA-400 resin on leach liquor obtained from 0·09 per cent U_3O_8 grade ore from Chhinjra gave a 50 per cent U_3O_8 grade sodium-di-uranate cake representing complete recovery of 76 per cent uranium taken into solution by the leach liquor.

Resin extraction tests with different types of resin for leach liquors obtained from ores of differing characteristics are now being carried out.

BACTERIAL LEACHING

A few words on bacterial leaching would not be out of place here. The main object of bacterial leaching is to reduce cost of acid, such as can also be done by autoclave leaching of sulphide ores or by formation of acid from sulphides by heap-leaching. *Thiobacillus ferroxidans* in the presence of iron sulphide minerals between 18 °C and 35 °C increases leachability of uranium by converting ferrous iron to ferric iron and formation of sulphuric acid. Ferric iron oxidizes the tetra-valent uranium to the hexavalent state enabling its dissolution (Fisher 1966). It has been noted that rate of extraction decreases logarithmically when plotted against time. In Yugoslavia, *Thiobacillus ferrobacillus* group of bacteria obtained from mine water, selected and cultivated, are thought to have some influence on leaching rate of uranium from low-grade ores (Buji 1966). The bacterial strains have to be adaptable to conditions resulting from the reactions between ore, moisture and air (Downes 1966). A good deal of preliminary investigation and culture of bacterial strains thus appears to be necessary for selection of bacteria which would be effective in a given environment. For this reason it has not been possible to experiment with bacterial leaching in our laboratories yet.

A period of 10 to 12 months is considered necessary for heap-leaching. It is to be noted that equivalent recoveries have been discovered in our investigations in a period not generally exceeding a month and, in some cases, in a day or a few days.

It is necessary in conclusion to draw attention to the high cost of sulphuric acid (Rs.400 per ton as against Rs.150 to Rs.200 per ton materially in Europe, etc.) in India which effects the economics of heap-leaching as it has already done in the case of other industries which depend on this essential chemical.

None the less, because of the general simplicity of the process, after the basic parameters for treatment of a given type of ore have been established in the laboratory, the avoidance of heavy capital outlay on equipment and cost of expensive technical supervision, heap-leaching or lixiviation, it seems to me, will come to be used extensively for extraction of uranium from the type of ore deposits mentioned earlier in the paper. This expectation may, perhaps, be extended in course of time to extraction of various base metals from small deposits scattered in different parts of the country which would otherwise remain unexploitable. The account just presented not only shows the progress achieved thus far in heap-leaching but its far-reaching future possibilities.

ACKNOWLEDGEMENT

I should like to express my appreciation here of the devoted work done by the officers of the Mineral Technology Laboratories without which the presentation of this work would not have been possible.

DISCUSSION

Question

Since uranium-bearing lignitic clay is friable, it is likely to present problems of percolation due to compaction in heaps. Has this problem been met and studied ?

K. D. AGRAWAL

Author's reply

Compaction of fine material in stacks is a well-known problem. This compaction is aided by wetting of the material or when it is submerged under a liquid. We are working on this problem as presented by the uraniferous clay bed at Neyveli. The two obvious solutions seem to be to use very thin layers of clay separated by coarse material in stacks, or by pugging the clay with acid and washing it with water to draw out uranium. We hope to be able to present the results of our investigations in the near future.

Paper: Progress in Heap-leaching Investigations on Different Types of Uranium Ores.

Author's name: K. K. Dar.

Questioner's name: D. V. Bhatnagar.

Comments

Heap and percolation leaching techniques have been employed in various parts of the world for the recovery of uranium. Some interesting data have been presented on some of the Indian ores by Mr. Dar and his band of workers. At Jadugoda also some studies are in progress in the recovery of uranium by percolation leaching from ore, below-the-cut-of-grade, which will be raised to the surface and is proposed to be sent to the waste dumps. While conducting percolation or heap-leaching studies, economic aspects of uranium recovery must be kept in view and studies on a large scale and putting up of large plants should be undertaken only after economic feasibility studies have been made. I would like to give an example where percolation leaching technique has not given the desired results. In Sweden, after very good laboratory studies on the uraniferous shales, an elaborate flowsheet employing ore dressing, weathering and percolation leaching techniques was evolved and a full-scale plant with a capacity of 3,000 tonnes per day was put up to treat a low-grade ore assaying about 0·03 per cent U_3O_8. Now the process has been found to be very uneconomical and I understand that either the plant has been shut down or is operating at only 10 per cent of its rated capacity.

It has been mentioned at this symposium that some samples of low-grade uraniferous ores from India have been sent to Prof. Kilstadt of Sweden for uranium recovery studies. In view of the fact that Swedish scientists and engineers have not been able to recover uranium economically from their own very vast resources, it should not be presumed that they will find economical processes for the ores sent by us.

D. V. BHATNAGAR

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FLOTATION OF LOW GRADE URANIUM ORES WITH ISO-OCTYL PHOSPHATES

by K. V. VISWANATHAN, S. K. SHUKLA *and* K. K. MAJUMDAR,
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(*Received 29 April 1969*)

Low grade uranium ores from Singhbhum Thrust Belt containing uraninite as the principal uranium bearing mineral have been earlier successfully beneficiated by flotation using iso-octyl acid phosphate. The ore under investigation also obtained from the same area contained about 0·05 per cent U_3O_8 as uraninite and 38 per cent chlorite. About 16 per cent of the total uranium values are intimately associated with the latter and another 16 per cent are associated with other gangue minerals principally magnetite (8–9 per cent). Iso-octyl phosphate is not only a very good collector for uranium minerals but it also acts as a collector for chlorite and magnetite. However, by repeated cleaning operation of the flotation concentrate, these gangue minerals can be discarded but at the expense of uranium values. The following alkyl phosphates were prepared and used for flotation of low grade uranium ores: (*a*) Normal and iso-octyl phosphates, (*b*) Lauryl phosphates, (*c*) *n*-Oleyl phosphates, (*d*) *n*-Adol phosphates. Flotation of low grade uranium ores (0·02–0·05 per cent U_3O_8 eq) with iso-octyl acid phosphates and *n*-octyl acid phosphates at around a *p*H of 2·4 gave a concentrate assaying 0·14–0·168 per cent U_3O_8, with a recovery of 80–85 per cent. Under the same conditions C_{12}–C_{18} alkyl phosphates gave higher grade concentrates (0·22 per cent U_3O_8) but the recovery was only 70–75 per cent.

There have been many studies on the flotation of low grade uranium ores but in general flotation of uranium minerals from low grade ores has not been very successful. The collectors used by earlier workers were petroleum sulphonate (Lord and Light 1956; Morris and Butler 1956), dithiocarbomates (Jackson 1955) and emulsified anionic reagents (Madhavan *et al.* 1963) (like oleic acid, sodium oleate, napthenic acid, sulphonated castor oil, etc.). However, when using these reagents as collectors, some minerals like chlorite, biotite and apatite occurring in the ores, which were more easily flotable with these reagents, floated with the uranium minerals and prevented a high enrichment ratio.

Phosphates form various complexes with uranium minerals and so it was felt that an organic phosphate might be used as a specific collector for uranium bearing minerals. Alkyl acid phosphates and their alkali salts were first used for the flotation of pitchblende ores (Eigeles *et al.* 1958). Successful flotation of uranium minerals like brannerite, uranothorite (Somnay and Light 1963) and uraninite (Viswanathan and Somnay 1967; Degaleesan *et al.* 1968) was also reported using iso-octyl acid phosphates or *n*-octyl acid phosphates as collector.

The present paper incorporates the flotation results of the uranium bearing mineral uraninite from the low grade uranium ores from Bhatin, Rakha mines and Narwapahar, all from Singhbhum Thrust Belt.

MATERIALS

Bhatin Ore: The mineralogical composition of Bhatin ore is (wt percentage): Quartz—55, Chlorite—9·6, Pyrite and Chalcopyrite—3, Apatite—3·7, Tourmaline and other minerals—0·6. The ore assayed 0·03 per cent U_3O_8 by radiometric method and the principal uranium bearing mineral was uraninite.

Rakha Mines Ore: The copper ores from Rakha mines of Bihar contain 0·02 per cent U_3O_8. The mineralogical composition of the ore is (wt percentage): Quartz—85, Micas—6, Sulphides—3·8, Magnetite—4·0 and others—1·2.

Nawapahar Ore: This ore is from a chlorite bearing quartz schist and contains 0·055 per cent U_3O_8. The mineralogical composition of the ore is (wt percentage): Quartz—51·0, Chlorite—38·0, Apatite—4·8, Magnetite—4·3 and others—1·85. The chlorite content in this ore is four times higher than that of the Bhatin ore and six times higher than that of the Rakha mines ore. Mineralogical analysis of the ground product indicated that 90 per cent of the uranium values will be liberated if the ore is crushed to 25 μ.

PREPARATION OF FEED

The ores were initially crushed to −10 mesh in a laboratory roll crusher. They were then wet ground in a rod mill to obtain the required final product for flotation. Preliminary flotation tests with ores ground to different fineness gave an indication of the optimum grind.

In the case of Bhatin ore the ore was ground to all −100 mesh and in the case of Rakha mines ore the ground material was 45 per cent passing through 200 mesh. In the case of Narwapahar ore the material was ground to 70 per cent passing through 200 mesh.

FLOTATION PROCEDURE

The ground ores were floated in a laboratory Denver type flotation cell using a charge of 0·5 kg or 1·5 kg (dry basis). The pulp density was maintained at 17–18 per cent solids during flotation. Sulphuric acid was used for *p*H adjustments.

TABLE I

Feed : 500 g. Conditioning times : 5 minutes. Pulp density : 17% solids

Collector	Amount of collectors in kg/t.	*p*H	Concentrate			Tailings			Selectivity Index
			% Wt.	% U_3O_8	% Dist. U_3O_8	% Wt.	% U_3O_8	% Dist. U_3O_8	
BHATIN ORE:									
Oleic acid	9	4·8	43·0	0·064	77·6	57·0	0·0140	22·4	2·13
Petroleum sulphonate	12	2·0	47·0	0·062	79·4	53·0	0·0140	20·6	2·08
Mixture of mono and di *n*-octyl phosphoric acid (1 : 1)	10	2·0	24·1	0·120	82·5	75·9	0·0078	17·5	3·91
Mixture of mono and di *n*-octyl phosphoric acid as per Breymann's method (1 : 1) ..	9	2·0	26·7	0·120	8·1	73·3	0·0067	13·9	4·17
RAKHA MINES COPPER ORE:									
Oleic acid	0·72	3·8	22·6	0·027	37·5	77·4	0·0130	62·5	1·43
Petroleum sulphonate	2·00	3·1	37·1	0·041	70·4	62·9	0·0140	29·6	2·00
Iso-octyl acid phosphates (mixture of mono and di)	12·60	1·6	17·8	0·100	95·7	82·2	0·0016	4·3	10·00
	10·80	1·9	43·0	0·039	90·8	57·0	0·0036	9·2	3·38
	23·20	1·3	14·1	0·120	94·2	85·9	0·0018	5·8	9·35
Iso-octyl acid phoshates	2·00	1·6	12·8	0·150	88·0	87·2	0·0030	12·0	7·06
Diesel oil	0·10								
Dodecyl sulphate	0·03								
Aerosol	0·01								

TABLE II

Feed : 1·5 kg. Conditioning time : 10 minutes. Pulp density : 17% solids

Collector	Amount of collectors in kg/t.	*p*H	Concentrate % Wt.	Concentrate % U_3O_8	Concentrate % Dist. U_3O_8	Tailings % Wt.	Tailings % U_3O_8	Tailings % Dist. U_3O_8	Selectivity Index
NARWAPAHAR ORE									
IOAP (mixture of mono and di)	8·0	2·5	26·4	0·168	83·0	73·6	0·012	17·0	3·70
NOAP (mixture of mono and di)	8·0	2·5	39·0	0·120	83·5	71·0	0·015	16·5	2·85
IOAP (mixture of mono and di)	8·0								
Diesel oil	2·0	2·5	36·0	0·130	84·0	64·0	0·014	16·0	3·08
Cresylic acid	2·0								
Lauryl sulphate	0·3								
Oleic acid (OA)	99·0	3·8	21·6	0·130	54·5	78·4	0·031	45·5	2·05
Oleic acid (OA)	20·0	4·6	33·0	0·105	69·3	67·0	0·025	33·0	2·07
Petroleum sulphonate	10·7	2·8	20·5	0·026	8·0	79·5	0·078	92·0	—
LAP (mixture of mono and di)	8·0	2·5	17·7	0·230	75·5	82·3	0·028	24·5	2·85
ADOLP	8·0	3·0	31·3	0·141	76·0	68·7	0·020	24·0	2·65
OAP	8·0	2·9	35·4	0·123	75·5	64·6	0·022	24·5	2·37

The Rakha mines copper ore (analysing 0·02 per cent U_3O_8 mainly occurring as uraninite) was initially floated for sulphide minerals using xanthates. The flotation tailings were subsequently used for uraninite flotation.

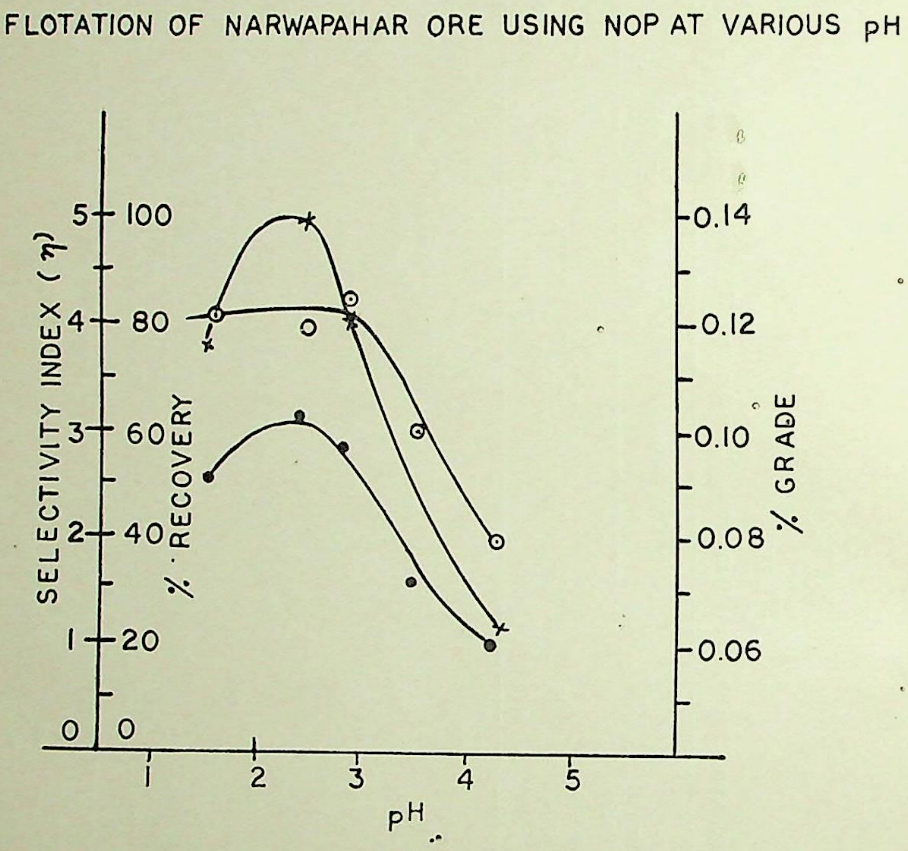

FLOTATION OF NARWAPAHAR ORE USING NOP AT VARIOUS pH

FIG. 1

Legend :

●—Selectivity Index

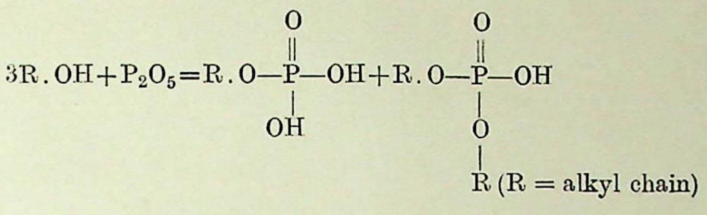
×—Grade

⊙—Recovery

$$\eta = \sqrt{\frac{\%U_3O_8 \text{ in the float}}{\%U_3O_8 \text{ in the tails}}}$$

PREPARATION OF FLOTATION COLLECTORS

The collectors were prepared by the method suggested by Breymann (1958) with some modification subsequently. To a known weight of phosphorous pentoxide (P_2O_5—6 gms) 25 ml of kerosene was added. To this slurry the fatty alcohol was added drop by drop until P_2O_5 was dissolved. The resulting product was diluted with acetone. But in order to reduce the cost of flotation reagent acetone was replaced by rectified spirit. Only a mixture of mono- and di-octyl acid phosphates is obtained by this method. The reaction can be represented as follows:



$$3R.OH+P_2O_5=R.O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-OH+R.O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\underset{\underset{\displaystyle R}{|}}{\displaystyle O}}{|}}{P}}-OH \quad (R = \text{alkyl chain})$$

Evaluation of Results

The form of the Selectivity Index used for calculations is as follows (Madhavan and Majumdar 1963):

$$\text{Selectivity Index } (\eta) = \sqrt{\frac{\%U_3O_8 \text{ in the float}}{\%U_3O_8 \text{ in the tails}}}$$

FLOTATION OF NARWAPAHAR ORE USING IOAP AT VARIOUS pH

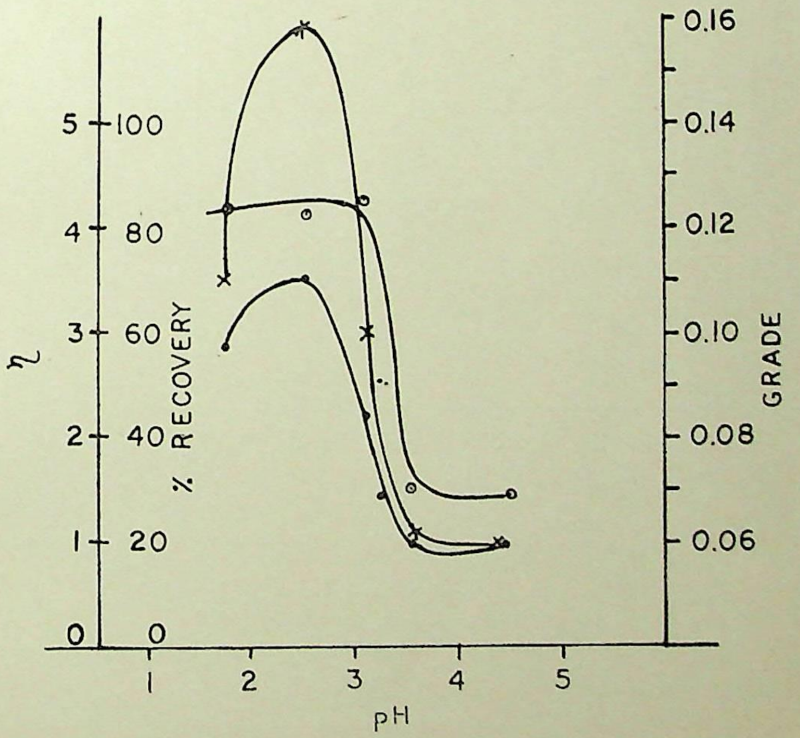


FIG. 2

Legend :

● —Selectivity Index

× —Grade

⊙ —Recovery

Results:

Table I summarizes the flotation results obtained in low grade, chlorite content Bhatin ore and tailings from Rakha mines copper ore. Table II incorporates the results obtained on Narwapahar ore. For comparison the experimental results carried out with other common collectors, viz. oleic acid (OA) and petroleum sulphonate (PS), are also included. In the case of Narwapahar ore, which contained a high amount of chlorite, other long chain acid phosphates containing C_{12}–C_{18} carbon atoms are also included. Figures 1–5 give the results of flotation on this ore with various alkyl acid phosphates at different *p*H values.

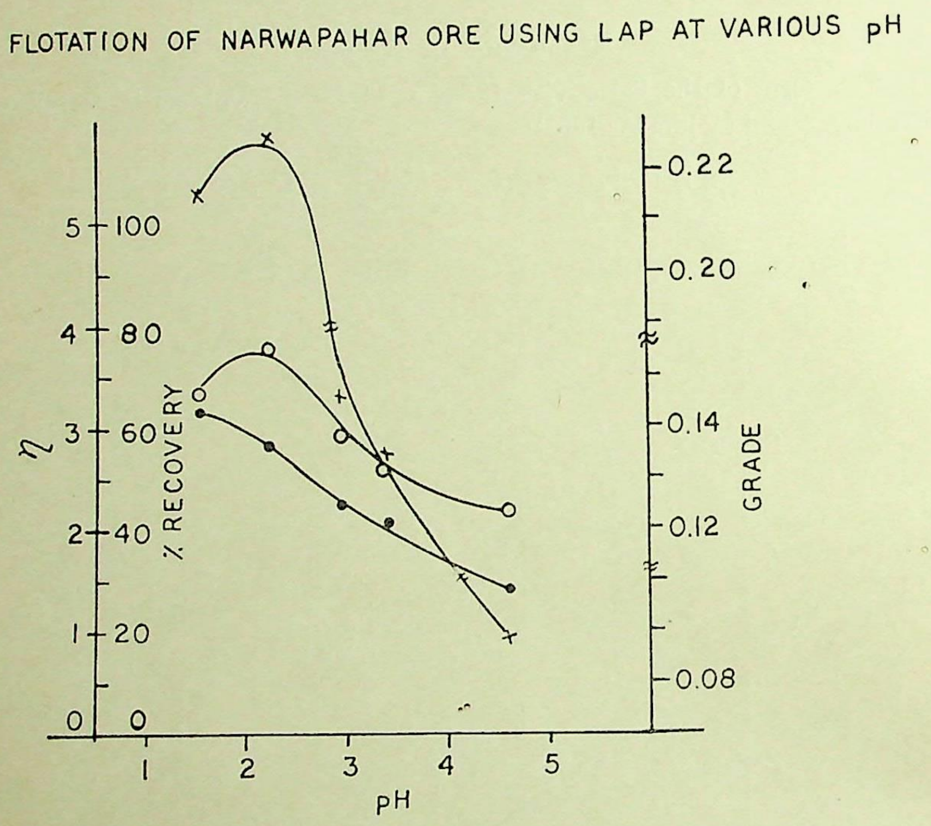

FLOTATION OF NARWAPAHAR ORE USING LAP AT VARIOUS pH

Fig. 3

Legend:

●—Selectivity Index
×—Grade
⊙—Recovery

DISCUSSIONS

From Tables I and II, it is seen that the optimum *p*H condition for the flotation of uraninite varies from ore to ore. The Selectivity Index is found to be the highest around 10 in the case of Rakha mines ore and between 2·5 and 3 in the case of Narwapahar ore. A mixture of mono and di *n*-octyl acid phosphates (1 : 1) was not selective beyond 6 *p*H in the case of Bhatin ore. The recovery figures were 80 per cent and above in the *p*H range 1·7–2·8 with more or less the same grade of the float, around 0·12 per cent U_3O_8.

It is seen from Figs. 1–5 that in the case of Narwapahar ore both the lower and higher aliphatic alkyl phosphates are found to be selective up to 3·5 *p*H. Within the homologous series the best flotation characteristics were displayed by iso-octyl acid phosphate. Using iso-octyl acid phosphate around a *p*H of 2·5, a grade as high as 0·168 per cent U_3O_8 is obtained with a

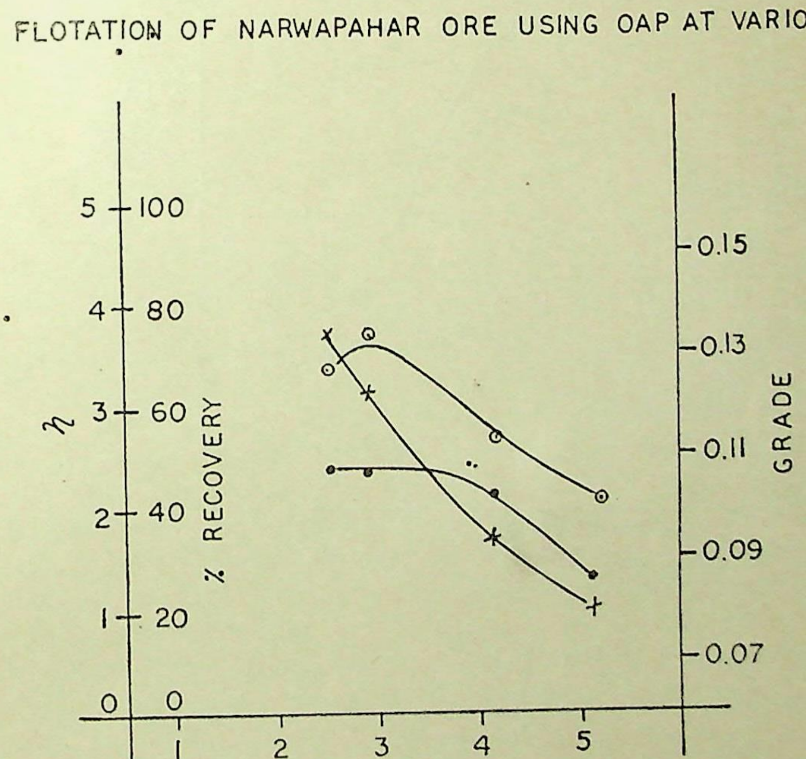


FIG. 4

Legend:

● —Selectivity Index

× —Grade

⊙ —Recovery

recovery of 83 per cent. Under the same conditions *n*-octyl acid phosphate gave a grade of 0·14 per cent U_3O_8 with 80 per cent recovery. Among the flotation reagents tried Lauryl acid phosphates gave the highest grade of 0·22 per cent U_3O_8 at 2·5 *p*H, but the recovery was only 75·5 per cent. Oleyl phosphate which is having a double bond in the alkyl chain gave a grade of 0·13 per cent U_3O_8 with 70 per cent recovery. ADOL phosphate gave a grade of 0·14 per cent U_3O_8 with 75 per cent recovery.

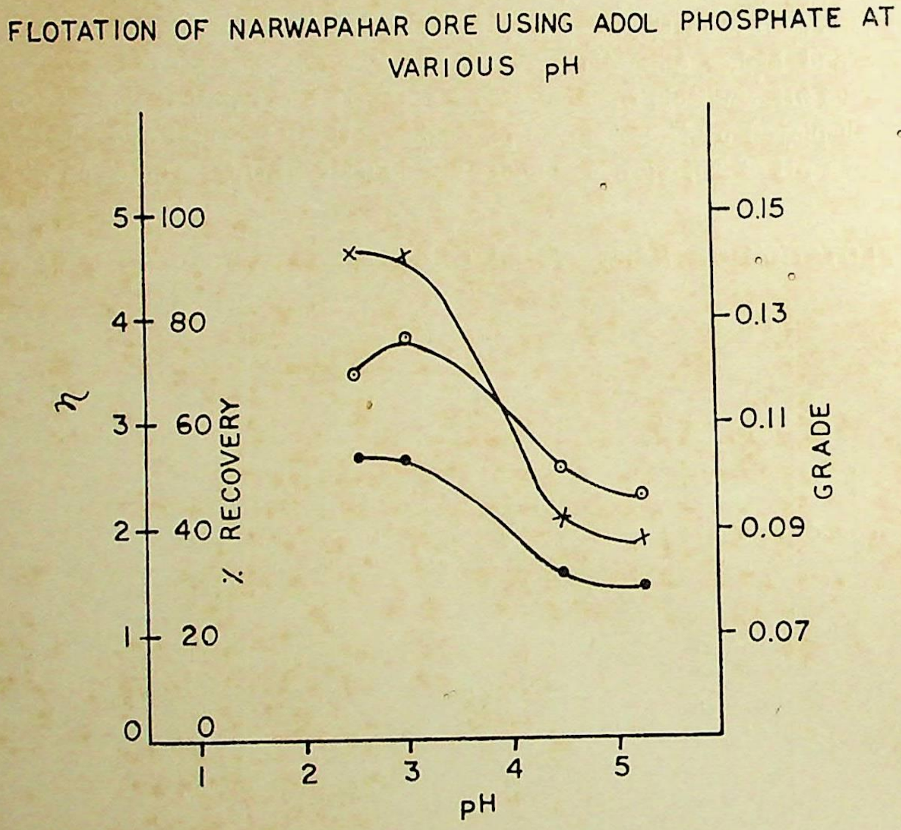


FIG. 5

Legend :

● —Selectivity Index
× —Grade
⊙ —Recovery

The recovery figures remained constant between 1·5 and 3·2 *p*H in the case of *n*-octyl acid phosphate and iso-octyl acid phosphate but the grade was maximum only around 2·5 *p*H. In the case of Lauryl acid phosphate the optimum *p*H was found to be around 2·5 and it was around 3 *p*H in the case of oleyl acid phosphate and ADOL phosphate. Increasing the alkyl chain length, thus resulted in the higher grade of uranium in the float but at the cost of recovery.

Because of the low *p*H required for flotation the reagent consumption is found to be very high. However, the flotation studies on Rakha mines uraninite as shown in Table I indicated that an emulsion of iso-octyl acid phosphate, diesel oil, dodecyl sulphate (DDS) and Aerosol reduced the reagent consumption considerably. In the case of Narwapahar ore (viz. Table II) consumption of iso-octyl acid phosphate was reduced to half using an emulsion of DDS, diesel oil and cresylic acid.

Radiometric analysis of the individual minerals present in the Narwapahar ore is shown in Table III.

TABLE III

Mineral	% St.	% U_3O_8 eq	% Distribution
Quartz	50·0	0·004	4·0
Chlorite	40·0	0·020	16·0
Apatite	4·0	0·017	1·3
Magnetite ..	4·15	0·100	8·4
Other sulphide minerals	1·85	0·077	2·9
	100·00	0·0163	32·6

The results indicate that uranium loss due to magnetite, chlorite and sulphide minerals is of the order of 32·6 per cent.

Autoradiographs of uraninite, magnetite and (unfloated) chlorite particles are given in Fig. 6. From the figure it is clear that activity is locked up in the case of magnetite as radioactive coatings (Fig. 6(*a*)) and also as lattice substitution of uranyl ion for Fe^{++} ions (Fig. 6(*b*)). Autoradiograph of completely liberated uraninite particles is given in Fig. 6(*c*). The activity is locked up in the case of chlorite as opaque inclusions (Fig. 6(*d*)) and also as small opaque inclusions showing activity on one part of the chlorite grain. Very fine uraninite particles (Fig. 6(*e*)) were also carried down along with large chlorite particles. The loss of uranium in the tailings can be attributed to all these factors.

CONCLUSIONS

1. Uraninite can be successfully floated from low chlorite as well as from high chlorite content low grade uranium ores (U_3O_8 eq 0·02 to 0·05) using iso-octyl acid phosphates and *n*-octyl

acid phosphates as collectors at a *p*H around 2·5 with recovery about 80–85 per cent, the grade of concentrate being 0·14 per cent to 0·168 per cent U_3O_8.

2. C_{12}–O_{18} alkyl fatty phosphates gave high grade concentrate (U_3O_8—0·22 per cent) but the recovery was only of the order of 70–75 per cent.

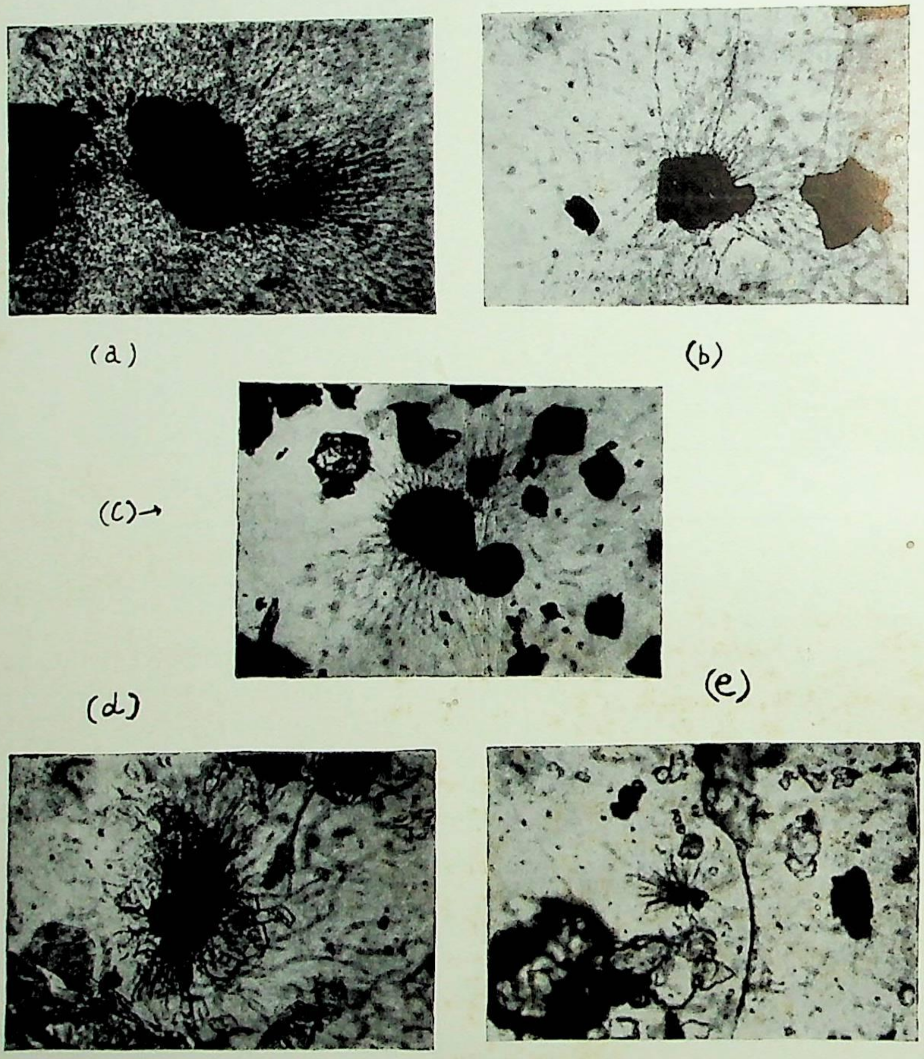


FIG. 6. (*a*) Radioactive coatings on magnetite (×230); (*b*) Radioactive magnetite (×230); (*c*) Fully liberated uraninite (×110) particle; (*d*) Opaque inclusions in chlorite (×230) showing activity; (*e*) Small uraninite particle (showing activity) with large chlorite particles (×230).

APPENDIX

Formulae of the Reagents

1. $C_8H_{17}H_2PO_4$ m–*n*-Octyl Acid Phosphate (m–NOP)
2. $(C_8H_{17})_2HPO_4$ Di–*n*-Octyl Acid Phosphate (Di–NOP)
3. C_4H_9—$CH(C_2H_5)$—$CH_2H_2PO_4$ m–iso Octyl Acid Phosphate (m–IOP)
4. $(C_4H_9$—$CH(C_2H_5)$—$CH_2)_2HPO_4$ Di–iso Octyl Acid Phosphate (Di–IOAP)
5. $C_{12}H_{25}H_2PO_4$ m–Lauryl Acid Phosphate (m–LAP)
6. $(C_{12}H_{25})_2$ HPO_4 Di–Lauryl Acid Phosphate (Di–LAP)
7. C_8H_{17}—$CH=CH$—C_8H_{16}—H_2PO_4 m–Oleyl Acid Phosphate (m–OAP)
8. $(C_8H_{17}$—$CH=CH$—$C_8H_{16})_2HPO_4$ Di–Oleyl Acid Phosphate (Di–OAP)

ACKNOWLEDGEMENTS

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RESULTS OF SOME BENEFICIATION AND LIXIVIATION TESTS ON MEDIUM-GRADE URANIUM ORE IN QUARTZITE FROM CHHINJRA, KULU DISTRICT, HIMACHAL PRADESH

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Beneficiation tests on medium-grade uranium ore, analysing 0·10% U_3O_8, from Chhinjra showed that, as compared to the low grade ore (0·032% U_3O_8) from the area, uranium distribution in the sieved fractions is higher in the coarser sizes upwards +60 mesh (A.S.T.M.), and tabling yields a concentrate assaying 0·94% eU_3O_8 from a −100 mesh feed assaying 0·12% eU_3O_8 at a low recovery of barely 21%, and anionic flotation of deslimed feed at −200 mesh (A.S.T.M.) yields a concentrate analysing 0·82% eU_3O_8 at 77·5% recovery.

In order to reduce the cost of grinding to fine sizes and loss of uranium in physical beneficiation, agitation and percolation leaching tests were tried; the latter yielding better results than the former. Leachability increased from 36·0 per cent without oxidant to 81·0 per cent with the use of 10 lb/ton of MnO_2, the main function of the latter being to oxidize ferrous iron to ferric iron which, in turn, oxidized tetravalent uranium to the soluble hexavalent uranium. Removal of magnetics (0·10 wt. per cent) from the sample decreased the leachability to 75 per cent consequent on the decrease in the quantity of iron which was otherwise available for oxidation.

INTRODUCTION

The Chhinjra uranium ore analysing 0·11 per cent U_3O_8 was found to consist of hard, compact quartzite which besides 88·16 per cent quartz contains tourmaline, pyrite (1·54 per cent) and 0·1 per cent magnetics (Jayaram *unpublished report*).

The quartzite is traversed along fractures by veinlets of uraninite. Much of the uraninite occurs along these fractures as hard 'paint' or as coatings on the quartz grains, the latter being, in part, replaced by it. Besides the uraninite, coatings of a ferruginous matter and *smears* of secondary uranium minerals are also observed, especially in the phyllite. The ferruginous coatings were also found to be radioactive. Little uraninite, if any, occurs in the associated phyllite (Bhattacharyya *unpublished report*).

EXPERIMENTAL

Beneficiation Tests:

Sieve analysis of samples, radiometrically assaying 0·032 to 0·22 per cent eU_3O_8 ground to −20 mesh (A.S.T.M.), indicated that the uraniferous minerals in these samples are uniformly distributed in all the fractions of the low grade ore whereas the high grade vein material shows, as is to be expected, preferential concentration in the coarser sizes upwards of +60 mesh (Table I).

TABLE I

Sieve analysis at —20 mesh (A.S.T.M.)

Locality ..	Shangshan			Shangshan			Dhara-Khanora-Nal		
Assay value of feed ..	0·032% eU_3O_8			0·10% eU_3O_8			0·22% eU_3O_8		
% eU_3O_8 mesh (A.S.T.M.)	Wt. %	% eU_3O_8 grade	% Dist.	Wt. %	% eU_3O_8 grade	% Dist.	Wt. %	% eU_3O_8 grade	% Dist.
— 20 + 30	15·5	0·027	12·9	14	0·14	19·3	7·5	0·52	16·0
— 30 + 40	13·5	0·027	11·30	15	0·14	20·6	5·64	0·61	14·0
— 40 + 60	14·5	0·027	14·7	8	0·14	11·1	5·64	0·48	11·5
— 60 +100	12·5	0·030	11·6	10	0·20	19·7	8·06	0·32	10·9
—100 +140	9·0	0·025	6·9	13	0·029	3·6	17·77	0·14	10·5
—140 +200	4·0	0·025	3·1	40	0·065	25·6	12·09	0·10	5·1
— —200	31·0	0·041	39·5	–	–	–	43·54	0·17	31·4

TABLE II

Tabling of Chhinjra ore

Feed assay: 0.10 per cent eU_3O_8

Feed size (A.S.T.M.)	Concentrate		Tailings		Slimes	
	Grade % eU_3O_8	% Dist.	Grade % eU_3O_8	% Dist.	Grade % eU_3O_8	% Dist.
—200 mesh	1·80	34·6	0·096	31·7	0·12	33·9
—100 mesh	0·94	20·8	0·077	50·0	0·17	29·1
— 60 mesh	0·50	19·4	0·108	75·5	0·027	5·2
— 20 mesh	0·25	75·0	0·034	12·5	0·038	12·5
— 60 mesh	0·50 } 0·70	19·4 } 48·4	–	–	–	–
Tails of 5 ground to —100 mesh	0·95 }	29·0 }	0·069	46·4	0·027	5·2

Tabling:

Tabling tests carried out on samples ground to —200 mesh indicated that some amount of upgrading in the table concentrates and slimes is possible, but at less than 50 per cent recovery, the middlings and tailings seldom attaining a rejectable grade (Table II). Tabling at —60 mesh followed by retabling of tails ground to −100 mesh gave a concentrate analysing 0·70 per cent eU_3O_8 at an overall recovery of 48·4 per cent (Table II).

Tabling of the ore at −100 mesh followed by flotation of table tails ground to −200 mesh yielded a combined concentrate analysing 0·24 per cent eU_3O_8 at a recovery of 83·4 per cent (Table III).

TABLE III

Tabling and flotation of table tails
Feed assay: 0·12 per cent eU_3O_8

Size (A.S.T.M.)	Nature of concentrate	Grade % eU_3O_8	% Wt.	% Dist.
−100	Table concentrate	0·94	3·0	23·4
−100	Table slimes	0·17	21·0	29·6
−200	Flotation concentrate	0·20	11·4	18·9
−200	Flotation slimes	0·21	6·5	11·3
−200	Tails	0·035	57·5	16·6
			99·4	99·8

Flotation:

Anionic flotation of 0·1 per cent eU_3O_8 feed at −200 mesh (A.S.T.M.) size in an acid circuit yielded concentrates analysing eight times the feed value at only 77 per cent recovery (Table IIIA).

Leaching Tests:

In order to reduce costs of grinding the ore to fine sizes, reduce losses in tabling and flotation, and to recover as much uranium as possible, preliminary agitation leaching tests were carried out on samples ground to −60 mesh (A.S.T.M.). In these over 90 per cent of uranium was leached with 120·0 lb/ton of H_2SO_4 at ambient temperatures.

Percolation leaching tests to reduce acid consumption and eliminate cost of agitation were tried on different feed sizes. Other parameters studied were: height of stacks, strength of acid solution, percolation rate, quality and quantity of acid solution loaded at each stage, effect of oxidant and *p*H, etc.

PROCEDURE

The feed was ground to −5 mesh size and treated in a polythene container with 100 c.c. of 3 per cent H_2SO_4. Acid was then drawn by percolation. The leach liquor obtained was recirculated after curing the stack till it was

TABLE IIIA

Flotation of Chhinjra ore

Feed assay: 0·10 per cent eU_3O_8

Reagents used		Conditions							Concentrate		Middlings		Tailings	
		Feed size	C. *p*H	F. *p*H	% C.P.D.	% F.P.D.	Cond. time	Flot. time	% eU_3O_8 grade	% Dist.	% eU_3O_8 grade	% Dist.	% eU_3O_8 grade	% Dist.
R 801: H.F.:	1·5 lb/ton 0·2 lb/ton	−100	2	5·5	60	30	3′	1′	0·40	40·00	–	–	–	60·0
R 801: R 825: Na_2CO_3:	2 lb/ton 1 lb/ton *p*H: 7·5	−100	2	7·5	70	30	1′	1′	0·45	45·0	–	–	0·06	55·0
Oleic acid: H_2SO_4:	2·0 lb/ton 3·6 lb/ton	−100	2	4·0	70	30	2′	30″	0·88	50·0	–	–	0·055	50·0
Oleic acid: H_2SO_4:	3·0 lb/ton 3·6 lb/ton	−150	2·5	4·7	70	30	2′	1′	0·61	38·0	0·50	12·0	0·58	50·0
H_2SO_4: Oleic acid: Na_2S:	6·0 lb/ton 3·0 lb/ton 4·0 lb/ton	−200	1·8	4·1	70	30	3′ 3′ 3′	1½′	0·82	77·5	0·47	8·0	0·037	14.5

unable to take up any more uranium. Finally, the stack was washed with water. In the second set of experiments dilute H_2SO_4 of known strength was percolated through the stack for 7 hours and recirculated after allowing 17 hours' 'curing' time till maximum amount of uranium was extracted from the feed. The results of tests using various parameters are tabulated in Table IV, which shows that 81·0 per cent of uranium in the ore could be leached in 24 days with 54 lb/ton of 3 per cent H_2SO_4 and 10 lb/ton of MnO_2.

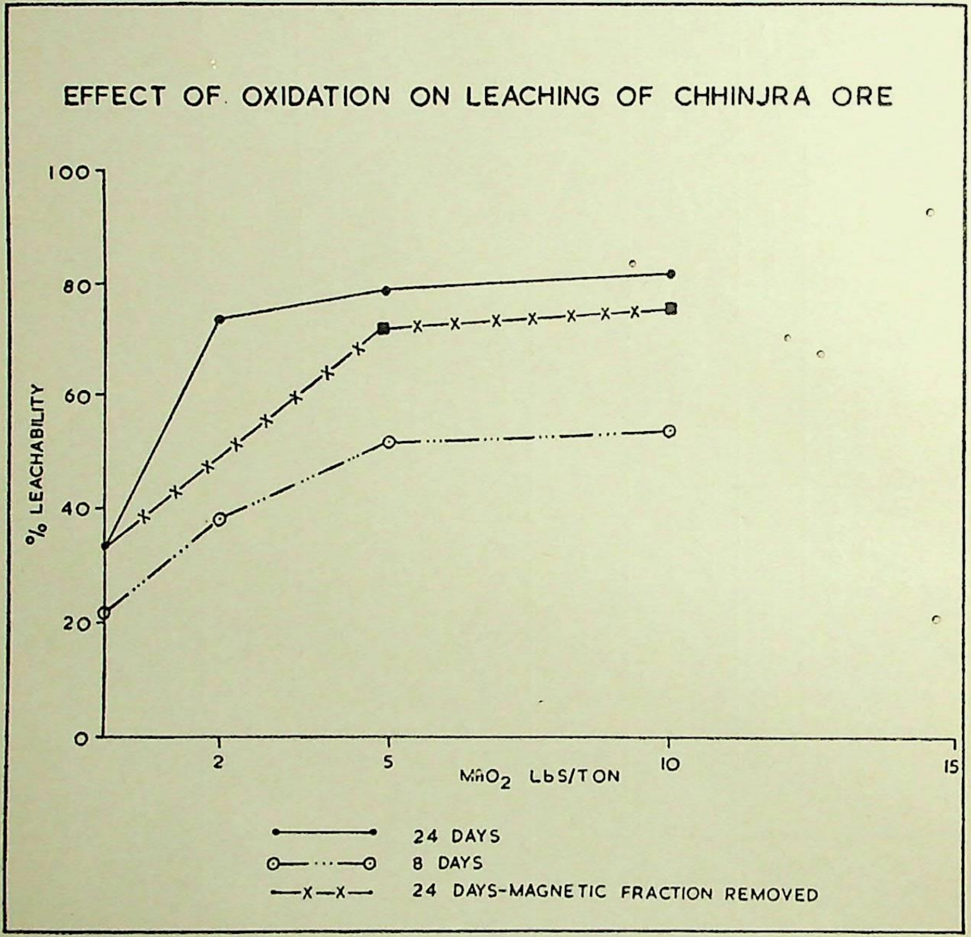

FIG. 1

Table V shows that with the removal magnetics from the ore the leachability decreased from 81·0 to 75·0 per cent because less ferric iron was formed which in turn limited the oxidation of tetravalent uranium to hexavalent state. Similarly addition of ferric iron helped the oxidation.

TABLE IV

Stack leaching of Chhinjra ore

Sl. No.	Size (A.S.-T.M.)	Assay per cent	Acid H_2SO_4		MnO_2 lb/ton	Curing hrs.	Leaching hrs.	Total days	Vol. of leach liquor c.c.	U_3O_8 Mg/l	% Leachability
			lb/ton	% Strength							
1	−5	0·10	54	3·0	nil	24 +48 +48	48 +48	8	200	210	21
2	−5	0·10	54	3·0	2·0	+48	+48	8	200	380	38·0
3	−5	0·10	54	3·0	5·0	+48	+48	8	200	520	52·0
4	−5	0·10	54	3·0	10·0	+48	+48	8	200	535	53·5
5	−5	0·10	54	3·0	nil	24	–	24	300	240	36·0
6	−5	0·10	54	3·0	2	24 +5×48 +24	48×6	24	300	490	73·5
7	−5	0·10	54	3·0	5	do	48×6	24	300	535	80·0
8	−5	0·10	54	3·0	10	do	48×6	24	300	540	81·0
9	−10	0·09	54	3·0	10	272	112	16	500	1050	58·0
10	−10	0·09	54	3·0	10	153	63	9	500	895	50·0
11	−10	0·09	54	3·0	10	323	133	19	500	990	56.0
12	−¼″	0·09	54	3·0	10	442	182	26	500	875	48·5
13	−¼″	0·09	54	3·0	10	578	238	34	500	1050	58·0
14	−10	0·10	30	1·0	15·0	80	40	5	–	20·7*	50·4
15	−10	0·10	80	3·0	20·0	64	32	4	–	17·6*	52·2
16	−10	0·10	60	1·0	18·0	96	48	6	–	18·2*	67·9

* Per cent U_3O_8 cake grade.

TABLE V

Effect of iron on the oxidation

Feed value: 0·10 per cent eU_3O_8

Sl. No.	MnO_2 loaded lb/ton	MnO_2 utilized lb/ton	Acid H_2SO_4		Time			Vol.	U_3O_8 mg/l	% Leachability
			lb/ton	% Strength	Curing hrs.	Leaching hrs.	Total days			
1	nil	nil	54	3·0	288	288	24	300	240	36·0
*2	nil	nil	54	3·0	288	288	24	300	245	36·5
3	5	4·0	54	3·0	288	288	24	300	538	80·0
*4	5	3·5	54	3·0	288	288	24	300	480	72·0
5	10	5·0	54	3·0	288	288	24	300	540	81·0
*6	10	4·5	54	3·0	288	288	24	300	500	75·0
†7	10	–	40	1·0	32	16	2	–	16·39‡	56·6
†8	15	–	40	1·0	32	16	2	–	17·0‡	62·9

* Magnetics removed.

† $Fe(SO_4)_3$ added @ 4 lb/ton.

‡ Per cent U_3O_8 cake grade.

These experiments show that:

(i) One per cent H_2SO_4 and even thinner solutions yield better grade cakes than stronger solutions due to lesser dissolution of iron (Table IV, Sl. Nos. 14, 15 and 16).

(ii) While the feed size of −5 mesh (A.S.T.M.) has been observed to be suitable for the purpose of a reasonably high leaching of uranium from the ore, a certain minimum amount of fines (32 per cent of −140 mesh) in the stack facilitates quicker leaching. Grinding the ore to a size finer than −20 mesh leads to compaction of the ore after wetting and prevents percolation of the acid (Table IV).

(iii) Use of 5 lb/ton MnO_2 increases the leachability from 36 per cent to 80 per cent due to the oxidation of uranium and, therefore, reduces acid consumption, but excess of MnO_2 above 18·0 lb/ton raises the U : Fe ratio to well over 1 : 7 and reduces uranium leachability by its reprecipitation in the lower parts of the stack during downward percolation of the leach liquor by reacting with minerals containing ferrous iron, e.g. pyrite, magnetite, etc. (Table IV).

(iv) Within certain limits leachability increases with leaching time and curing period (Table IV).

(v) Removal of magnetics from the ore reduces the leachability from 81 per cent to 75 per cent because less ferric iron was formed which in turn limited the oxidation of tetravalent uranium to the hexavalent state. Due to this the quantity of MnO_2 actually used up in oxidation was reduced to 45 per cent, that is 5 per cent less of the original consumption of 50 per cent (refer Table V and Fig. 1).

In view of the factors explained above, it is necessary to ensure in actual bulk heap leaching practice that no parameter is extended beyond its critical point to get the maximum leachability and recovery.

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A PRELIMINARY STUDY OF THE DISTRIBUTION OF URANIUM AND THORIUM IN THE GRANITIC ROCKS OF SINGHBHUM

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Eighteen representative specimens of Singhbhum granite (including 12 from magmatic members and six from the Bahalda metasomatic series) and two specimens of soda-granite along the Copper Belt thrust zone were used for (*a*) fluorimetric determination of uranium, (*b*) neutron-activation analysis of thorium, (*c*) flame-photometric determination of K and Na in 15 specimens, (*d*) wet chemical analysis of major constituents in five specimens and (*e*) point-count modal analysis and optical determinations of the compositions of the constituent minerals, and computation therefrom of the major element chemical composition of the rocks.

The available data indicate (*a*) abnormal richness of uranium in all three suites of rocks (by a factor > 2), (*b*) abnormally low thorium content in all the rocks except in soda-granite and (*c*) abnormally low Th/U ratios, the averages being 1·29, 1·01 and 2·36 for the magmatic members, Bahalda metasomatic series and soda-granites respectively.

In the magmatic units of Singhbhum granite, thorium shows fairly consistent positive correlations with Larsen Index, K % and Si %, while uranium shows only poor correlations with the above parameters; also in such rocks, the Th/U ratio shows highly significant positive correlation with the ratio $\left(\frac{Fe_2O_3}{FeO+Fe_2O_3}\right)$; all specimens with $Th/U < 1$ have $\left(\frac{Fe_2O_3}{FeO+Fe_2O_3}\right) < 0{\cdot}4$, whereas all those with $Th/U > 1$ have $\left(\frac{Fe_2O_3}{FeO+Fe_2O_3}\right) > 0{\cdot}4$. It is suggested tentatively that in parts of the magma with low oxygen pressure, the crystallizing rocks incorporated abnormally small amounts of thorium, leading to low Th/U ratios. In parts of the magma with higher oxygen pressure, uranium was partly leached out with the vapour phase or hydrothermal solutions and redistributed within the entire granite body, leading to its rather erratic distribution.

In the Bahalda series of rocks which represents all stages of metasomatic granitization of hornblende schist to hornblende granodiorite, it appears that the uranium and thorium brought in by the granitizing fluids were preferentially incorporated in sphene, allanite and other accessory minerals leading to the erratic distribution of both these elements.

Introduction

In the course of the authors' (Saha *et al.* 1965, 1968) studies on the trace element distribution in the magmatic and metasomatic members of the H.

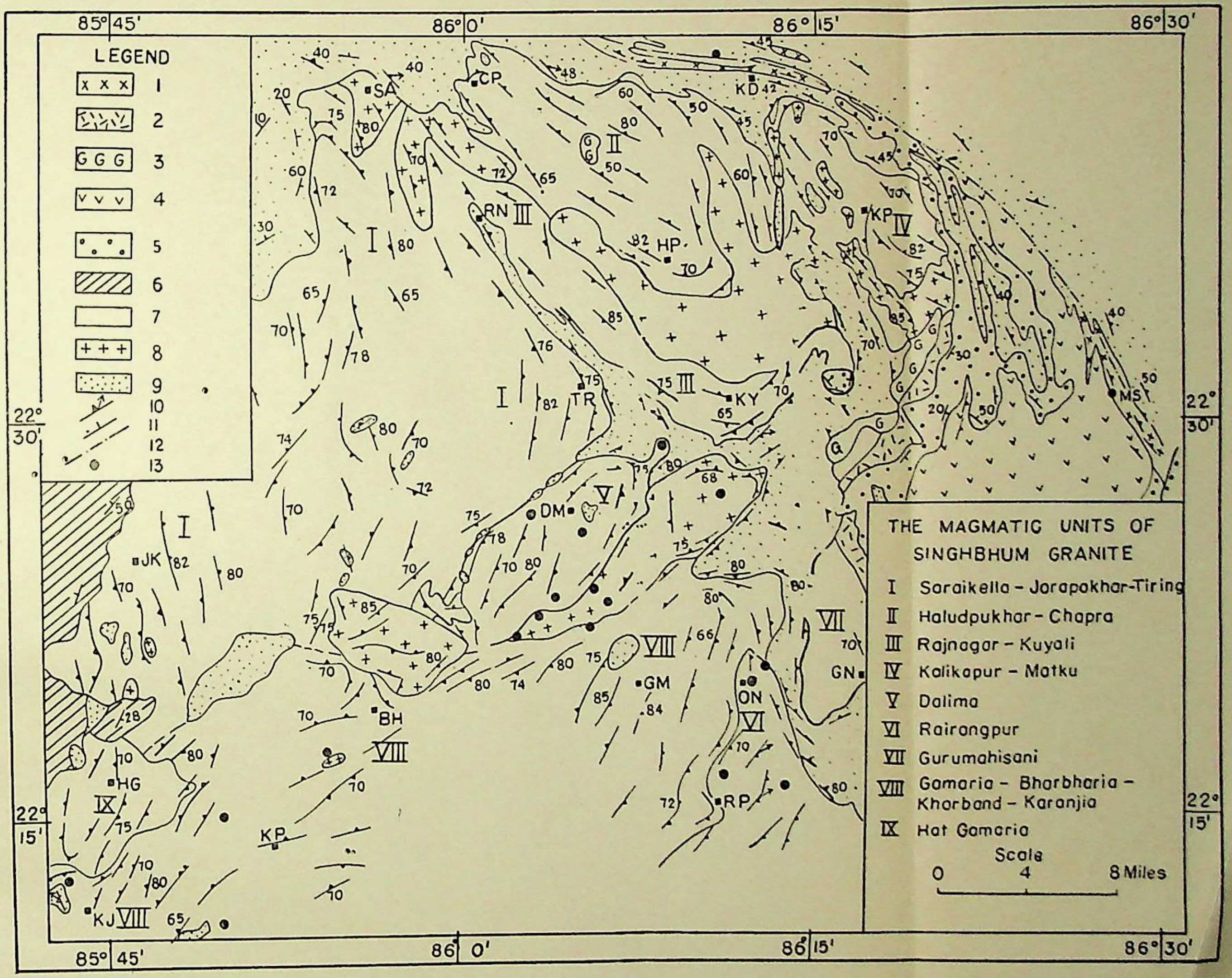

FIG. 1. Generalized geological map of the northern part of Singhbhum granite (after A. K. Saha 1966) with locations of the analysed specimens: 1, soda-granite and feldspathized schist; 2, granophyre; 3, gabbro; 4, Dhanjori lavas; 5, Dhanjori quartzite-conglomerate; 6, Kolhan series; 7, intrusive units of Singhbhum granitic complex; 8, metasomatites of Singhbhum granitic complex; 9, para- and orthometamorphic rocks (mostly of pre-Singhbhum granite age); 10, foliation and lineation; 11, bedding; 12, Copper Belt thrust zone; 13, location of the spectrochemically analysed samples. Important towns indicated thus: BH, Bharbharia; CP, Chapra; D, Dalima; GM, Gamaria; GN, Gurumahisani; HG, Hat Gamaria; HP, Haludpukhar; JK, Jorapokhar; KJ, Karanjia; KB, Khorband; KY, Kuyali; KP, Kalikapur; KD, Kudada; MS, Mushabani; RP, Rairangpur; RN, Rajnagar; SA, Saraikella; TR, Tiring.

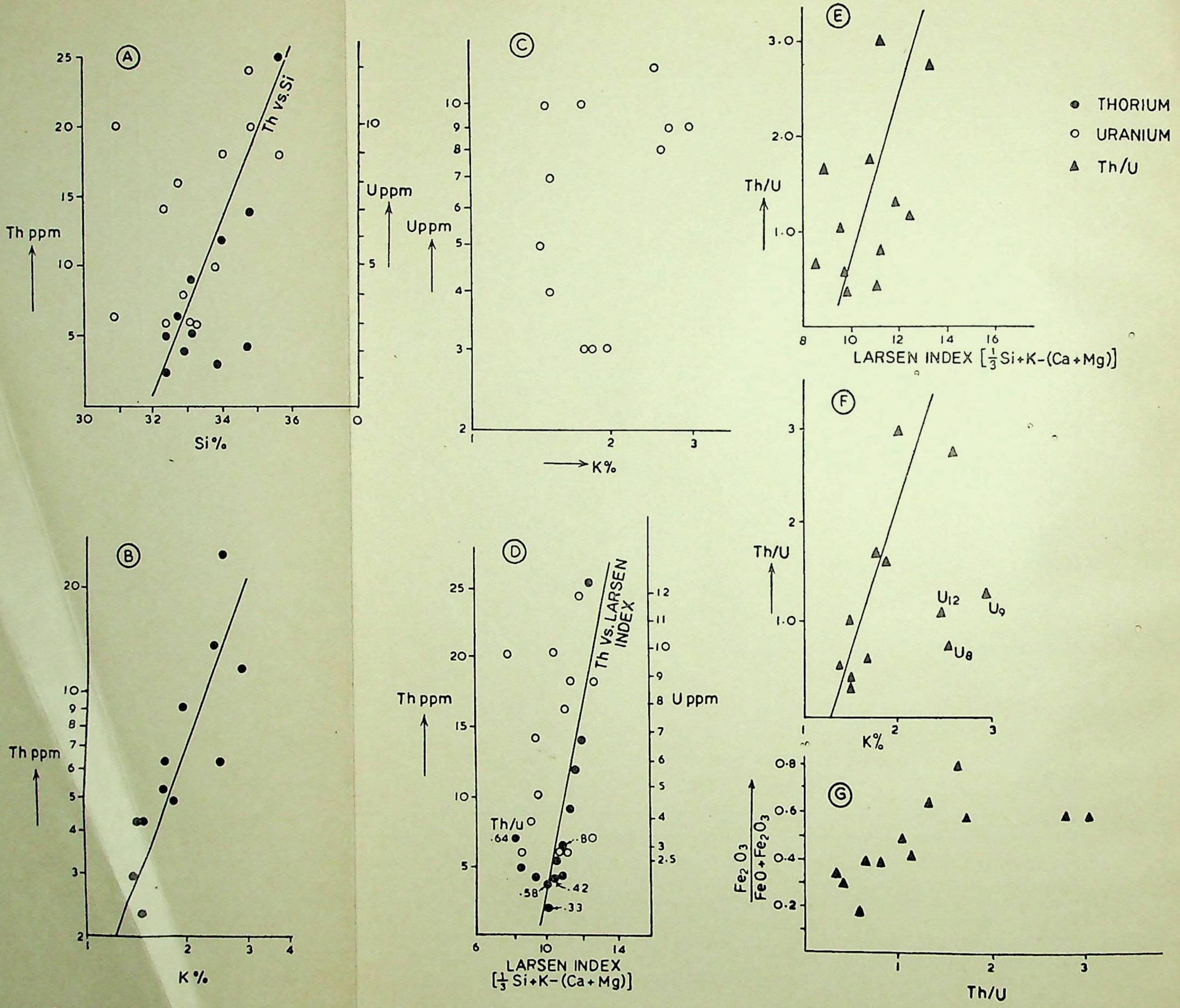

FIG. 2A–G. Diagrams showing correlations of uranium and thorium contents in the specimens of the magmatic units of Singhbhum granite with several chemical parameters of the rocks. (A) Th (ppm) vs. Si%; U (ppm) vs. Si%; (B) Th (ppm) vs. K%; (C) U (ppm) vs. K%; (D) Th (ppm) vs. Larsen Index; (ppm) vs. Larsen Index; (E) Th/U vs. Larsen Index; (F) Th/U vs. K%; (G) Th/U vs. $\frac{Fe_2O_3}{FeO+Fe_2O_3}$.

TABLE I

Point-count modal analyses of the specimens used for the study of U- and Th-distribution

(Data in weight, per cent)

Specimens and serial numbers	Magmatic units of Singhbhum granite																		Soda-granite	
	Phase I				Phase II				Phase III				Metasomatic unit							
	Dalima unit				Rairangpur-Onlajori				Bharbharia-Karanjia				Bahalda metasomatic unit							
	P 183	P 255	P 285	124 N	R 237	R 307	R 371	R 293	B 33/63	B 28/63	K 37/63	T 57	51 N	233 N	276 N	239 N	B 30/62	107 N	AT 20	T 252
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Quartz	19·8	29·5	22·4	31·3	27·6	26·8	26·5	27·8	35·5	32·2	36·3	42·7	×	3·9	12·9	14·5	18·1	24·7	38·9	34·3
Plagioclase	58·8	54·5	61·3	54·5	44·1	48·3	47·3	44·4	50·9	40·1	37·3	33·0	33·4	36·3	60·5	58·9	62·3	55·0	44·3	37·6
K-feldspar	5·3	5·1	7·4	5·7	13·4	16·1	17·3	14·4	6·6	17·2	19·0	15·4	1·5	3·1	1·3	8·9	0·1	9·5	–	–
Muscovite	×	×	×	×	×	×	×	0·2	0·5	1·3	1·1	0·8	–	–	–	–	–	–	5·5	10·5
Biotite	6·6	5·2	2·7	×	2·0	3·9	4·5	11·0	3·6	0·8	×	1·0	–	–	–	–	–	–	4·1	12·9
Chlorite	3·5	1·7	2·6	5·6	0·5	0·8	0·4	0·2	1·4	1·4	4·9	2·3	3·5	0·2	1·7	1·2	2·1	6·6		
Hornblende	–	–	–	–	–	–	–	–	–	–	–	–	54·3	54·0	19·7	11·8	14·7	1·1	–	–
Epidote-zoisite	5·4	2·6	2·3	2·6	10·3	1·6	2·3	1·2	1·0	6·5	0·9	1·8	6·0	1·4	3·1	2·9	1·3	2·6	×	0·6
Opaques	0·2	1·2	0·7	×	0·6	2·0	1·5	0·2	×	0·4	0·8	3·0	0·1	0·4	0·1	0·7	–	0·3	5·3	3·3
Sphene	0·5	0·2	0·3	0·3	0·8	0·3	0·1	0·3	×	0·1	tr	tr	0·2	0·6	0·5	1·0	1·3	0·2	1·9	×
Apatite				tr	0·6	0·2	0·1	0·2	0·1	×	×	×	0·3	–	0·2	tr	0·1	0·1		0·8
Zircon	×	×	×	tr	0·1	0·1	0·1	0·1	×	×	×	×	–	–	tr	tr	tr	tr		×
Total	100·0	100·0	99·7	100·0	100·0	100·1	100·1	100·0	99·6	100·0	100·3	100·0	99·3	99·9	100·0	99·9	100·0	100·1	100·0	100·0
An content of plagioclase	An_{23}	An_{25}	An_{24}	An_{22}	An_{22}	$An_{18·5}$	An_{17}	An_{23}	An_{22}	An_{21}	$An_{14·5}$	$An_{15·5}$	An_{25}	An_{20}	An_{16}	An_{20}	An_{23}	$An_{15·5}$	$An_{8·5}$	An_{15}

TABLE II

Thorium, uranium and some related chemical parameters in the granitic rocks of Singhbhum

(*See* text for Methods of Determination)

Sample numbers	Magmatic units of Singhbhum granite																		Soda-granite	
	Dalima unit				Rairangpur unit				Bharbharia-Karanjia unit				Bahalda metasomatic unit							
	P 183	P 255	P 285	124 N	R 237	R 307	R 371	R 293	B 33	B 28	K 37	T 57	51 N	233 N	276 N	239 N	B 30/62	107 N	AT 20	T 252
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Th ppm	6·4	4·2	2·3	2·9	4·9	5·2	9·1	6·4	4·2	11·9	13·7	25·0	2·2	12·6	9·6	7·3	9·4	7·6	19·0	23·4
U ppm	10	4	7	5	3	3	3	8	10	9	12	9	23	8	5	6	10	25	9	9
Si %	30·81	32·82	32·31	33·80	32·38	33·02	33·17	32·69	34·74	33·92	34·74	35·64	24·34	26·32	30·03	29·83	31·15	32·74	34·10	34·30
K %	1·72	1·49	1·50	1·41	1·82	1·77	1·98	2·56	1·46	2·97	2·47	2·58	0·82	1·13	0·85	1·58	1·05	1·83	2·17	2·20
Na %	3·55	3·38	3·80	3·19	2·95	3·63	3·48	3·11	3·40	2·68	2·72	2·43	2·64	2·78	3·84	2·80	3·62	3·47	2·33	2·55
Ca %	3·13	2·50	2·01	2·32	3·72	1·71	1·69	1·93	1·87	2·44	1·20	1·11	7·29	6·18	3·87	3·91	3·21	1·89	0·83	0·84
Mg %	0·78	0·49	0·55	0·63	0·24	0·36	0·31	0·42	0·36	0·20	0·47	0·33	4·78	4·45	1·78	1·24	1·43	0·84	0·47	0·38
Larsen Index	8·08	9·44	9·71	9·73	8·65	10·71	11·04	11·11	10·81	11·66	12·38	13·02	−3·14	−0·73	5·21	6·37	6·79	10·01	12·24	12·41
Th/U	0·64	1·05	0·33	0·58	1·63	1·73	3·03	0·80	0·42	1·32	1·14	2·78	0·10	1·58	1·94	1·22	0·94	0·30	2·11	2·60
$(Th/K) \times 10^4$	3·7	2·9	1·5	2·1	2·7	2·9	4·6	2·5	2·9	4·0	5·5	9·7	2·7	11·1	11·4	4·6	9·0	4·2	8·8	10·6
$(U/K) \times 10^4$	5·8	2·7	4·7	3·7	1·65	1·7	1·5	3·1	6·8	3·0	4·9	3·5	28·0	7·1	5·9	3·8	9·5	13·7	4·15	4·1
FeO	2·18	1·71	2·24	1·74	0·51	1·46	1·29	1·84	1·01	0·68	1·59	1·80	7·31	6·17	2·71	1·87	2·53	2·26	1·71	1·32
Fe_2O_3	1·35	1·57	1·13	0·33	1·76	1·92	1·68	1·15	0·41	1·18	1·09	2·39	4·18	3·16	1·45	1·45	1·52	0·60	3·18	1·78
$\frac{Fe_2O_3}{FeO+Fe_2O_3}$	0·38	0·48	0·33	0·16	0·78	0·57	0·57	0·38	0·29	0·63	0·41	0·57	0·36	0·34	0·35	0·44	0·37	0·21	0·65	0·58

Singhbhum granite as well as in the soda-granites of the Copper Belt thrust zone, it was noted that the uranium content of these granitic rocks are much higher (by a factor > 2) than normal granites. Thorium content of the rocks was not determined in these earlier studies.

A detailed knowledge of the geochemistry of uranium and thorium in these granitic rocks of Singhbhum is important for (*a*) understanding the ultimate source of uranium mineralization along the Copper Belt thrust zone and (*b*) providing clues for future search for uranium in the Singhbhum region.

The present paper reports the preliminary results of such studies which have been just started. Twenty specimens out of the suite of 56 granitic and associated rocks from the Singhbhum region, whose trace-element distribution had already been reported upon (Saha *et al.* 1965, 1968), were used for the present study. Out of these 20 specimens, 18 are from the Singhbhum granite batholithic complex, four each being from three magmatic units (Dalima, Rairangpur and Bharbharia-Karanjia units), which belong respectively to Phases I, II, and III of the intrusion sequence (Saha 1966); the other six specimens represent successive stages of metasomatic granitization of pre-existing basic metamorphics, as observed in the Bahalda metasomatic unit (Saha 1954; Saha and Chakrabarti 1963). Two of the specimens are typical soda-granites from the Copper Belt thrust zone, they represent a fairly advanced stage of soda-feldspathization of a group of mica schists and chlorite schists along the Copper Belt thrust zone (Banerjee 1957). As will be noted from the modal data (Table I), the 12 representatives of the magmatic members of Singhbhum granite are mostly biotite granodiorite with gradations to biotite-muscovite adamellite and leucogranite.

METHODS OF STUDY

Uranium in the above-noted 20 specimens was determined fluorimetrically by M. D. Shirgaonkar of Atomic Minerals Division while thorium was determined by neutron activation analysis at the Analytical Division of Bhaba Atomic Research Centre, Trombay, through the kind cooperation of V. T. Athavale. Full wet chemical major element analyses (by B. P. Gupta) are available for five of the specimens, while Na and K in the remaining 15 specimens were determined flame-photometrically at Presidency College by A. K. Saha in cooperation with P. K. Chattopadhyay. Major element chemical compositions of these 15 specimens were computed from the modal data, using certain assumed chemical compositions of the constituent minerals on the basis of their optical characters. As already noted (Saha 1966; Saha *et al.* 1968), such computed values correspond satisfactorily with the chemically analysed values, except for Na and K percentages, which were determined in all the 20 specimens directly by flame-photometry or by wet chemical method.

The percentages of the major elements in the 12 specimens of magmatic rocks were used to compute their Larsen Index $[\frac{1}{3}\ \mathrm{Si}+\mathrm{K}-(\mathrm{Ca}+\mathrm{Mg})]$, which is generally considered to be a good indicator of the progress of differentiation in magmatic sequences (cf. Ragland *et al.* 1957) (Table II).

The geological and geochemical significance of the data thus accumulated will now be discussed.

DISCUSSION OF RESULTS

The salient features of the U-Th distribution in this small suite of samples are as follows:

1. The magmatic as well as the metasomatic members of the Singhbhum granitic complex have abnormally low Th/U ratio. Whereas the average Th/U ratio in salic intrusive rocks is 3–4 (and only very rarely less than 1, cf. Adams *et al.* 1959), the average Th/U for the magmatic units of Singhbhum granite, the Bahalda metasomatic unit and the soda-granites are 1·29, 1·01 and 2·36 respectively, with as many as 40 per cent of the specimens having Th/U < 1.

2. The average uranium contents in all the three suites of rocks are much above the granite average of 4·75 ppm, while the thorium values are in general (except in the soda-granites) much below the granite average of 17·36 (cf. Heier and Rogers 1963). Thus the low Th/U ratios in the specimens of Singhbhum granite are due both to the abnormally high U and abnormally low Th values.

3. In the magmatic units of Singhbhum granite, Th values show good positive correlations with K %, Si % as well as with Larsen Index (Tables II and III; Fig. 2A, B and D). However, these correlations are feeble or absent for specimens with low Th values (< 7 ppm). Thorium appears to be absolutely uncorrelated with K, Si and Larsen Index in the Bahalda metasomatic series.

4. Uranium shows only low, statistically non-significant positive correlation with K, Si and Larsen Index in the magmatic units (Tables II and III; Fig. 2A, C and D). According to Larsen *et al.* (1956) a broad distribution pattern rather than a confinement to a narrow zone is expected in uranium values of granitic plutons. As in the case of thorium, uranium also appears to be absolutely uncorrelated with K, Si and Larsen Index in the Bahalda metasomatic series.

5. The Th/U ratio in the magmatic units shows fair (though statistically non-significant) positive correlations with K %, Si % and Larsen Index (Tables II and III; Fig. 2E and F). This ratio also shows highly significant positive correlation with the ratio $\left(\frac{\mathrm{Fe_2O_3}}{\mathrm{FeO}+\mathrm{Fe_2O_3}}\right)$ (Fig. 2G); the latter is generally considered to represent the 'oxidation state' of the rock (cf. Heier and Brooks 1966). Of considerable interest is the fact that all magmatic samples

TABLE III

Values of correlation coefficients (r) between certain chemical parameters in the magmatic members of Singhbhum granite (sample size = 12)

	Th (ppm)	U (ppm)	K (%)	Si (%)	$\frac{Fe_2O_3}{FeO+Fe_2O_3}$	Larsen Index
Th (ppm)	–	0·41	0·72 HS	0·60 S	0·35	0·82 HS
U (ppm)	–	–	0·14	0·32		0·44
Th/U	–	–	0·39	0·32	0·67 S	0·49 PS
$(Th/K) \times 10^4$	–	–	–	–	–	0·725 HS
$(U/K) \times 10^4$	–	–	–	–	–	−0·04 NS

—[after Snedecor (1957)]

$r_{0\cdot99} = 0{\cdot}708$; $r_{0\cdot95} = 0{\cdot}576$; $r_{0\cdot90} = 0{\cdot}455$;

HS = highly significant at the 99 per cent level; S = significant at the 95 per cent level;
PS = probably significant at the 90 per cent level.

with $Th/U < 1$ have $\frac{Fe_2O_3}{FeO_3+FeO} < 0{\cdot}4$, whereas all those with $Th/U > 1$ have $\frac{Fe_2O_3}{Fe_2O_3+FeO} > 0{\cdot}4$. It is significant also that in samples with $\frac{Fe_2O_3}{FeO+Fe_2O_3} < 0{\cdot}4$, thorium content is always less than 7 ppm. In the Bahalda metasomatic series, Th/U is uncorrelated with K %, Si % and Larsen Index, but here, too, samples with low Th/U (< 1) have low $\left(\frac{Fe_2O_3}{FeO+Fe_2O_3}\right)$ (< 0·4).

6. The ratio $(Th/K) \times 10^4$ shows highly significant positive correlation with Larsen Index, while the ratio $(U/K) \times 10^4$ is uncorrelated with the latter.

7. Although no autoradiographic or mineral-wise study of U-Th distribution in the present suite of rocks has been made, the abundance of pleochroic haloes around the accessory sphene and allanite in these rocks suggests that much of the uranium and thorium are locked up in sphene and allanite respectively. Adams *et al.* (1959; Table 5, p. 314) report that thorium content of allanite in igneous rocks has a range of 50–5000 ppm and uranium from 30 to 700 ppm with a Th/U between 5 and 10, while in sphene Th ranges from 100 to 600 ppm and U 100 to 700 ppm with a Th/U range of 1–2.

The fairly consistent relationship between thorium content on the one hand and Larsen Index, K % and Si % on the other as well as the significant correlation between $(Th/K) \times 10^4$ and Larsen Index in the magmatic series of Singhbhum granite suggest that the original Th content of the rocks has not been depleted or increased by redistribution during the late stages of crystallization or subsequent low-grade metamorphism. On the other hand, the lack of statistically significant correlation of uranium with Larsen Index or K % and its generally high values probably suggest the late stage enrichment and redistribution of uranium in these magmatic rocks.

Uranium and thorium are considered to occur in igneous rocks (i) as discrete minerals, (ii) as trace-element in minerals or (iii) in interstitial grain boundaries as loosely held 'Paint'. It has also been noted that a certain quantity of the uranium is easily leachable, giving rise to its erratic distribution. Uranium (U^{4+}) in many granitic magmas is partly oxidized to the more easily soluble hexavalent state, leading to its partial loss with the hydrothermal solutions or with the vapour phase (cf. Adams *et al.* 1959; Ragland *et al.* 1967), so that in such bodies uranium shows general decrease with increasing fractionation. In the magmatic units of Singhbhum granite, there is no general decrease of uranium with increasing fractionation, rather there is a feeble tendency of rising uranium with increasing Larsen Index (Table III; Fig. 2). This suggests that the hexavalent uranium in the late stage magma did not appreciably escape out of the granite body but was mainly redistributed within the granitic rocks themselves.

In respect of the low Th/U ratios and several other features, the magmatic members of Singhbhum granite resemble the white granite members of the Heemskirk granite in West Tasmania (Heier and Brooks 1966). In the latter, Th/U ratio ranges between 0·6 and 2·5, but unlike in Singhbhum granite (*a*) the low Th/U there is largely due to uranium enrichment (U, 12·5–27·4 ppm) with only a light depletion of thorium, and (*b*) there is negative correlation between Th/U ratio and $\left(\frac{Fe_2O_3}{FeO+Fe_2O_3}\right)$ ratio. Heier and Brooks (1966) suggested that low Th/U in magmatic sequences may appear (*a*) in rocks formed by crystallization of strongly differentiated rest magmas that have been produced under non-oxidizing conditions, or (*b*) in the late stage granites undergoing oxidizing conditions if the vapour phase does not escape appreciably into the surrounding rocks but is incorporated within the granite itself.

From a critical consideration of the available data on U-Th distribution in the magmatic members of Singhbhum granite, it appears that oxygen pressure in the magma played an important role as follows:

1. In parts of the magma with low oxygen pressure (as in Dalima unit), the crystallizing rock incorporated abnormally small amounts of thorium, leading to abnormally low Th/U ratios. In such rocks thorium values do not show any clear correlation with increasing fractionation. For reasons which are not yet clear, entry of thorium in minerals crystallizing from a granite magma seems to be impeded under conditions of low oxygen pressure. This is borne out also by the data of Heier and Brooks (1966).

2. In other parts of magma with higher oxygen pressure, uranium was partly leached out with the vapour phase or hydrothermal solutions and redistributed within the entire granite body, thus leading to its rather erratic distribution. Thorium, however, increased continuously with increasing fractionation, except in rocks with low oxidation ratio.

The erratic and often abnormally high values of uranium and thorium (particularly the former) in the Bahalda metasomatic series of rocks are explicable in terms of a hypothesis of preferential incorporation during progressive granitization of certain trace elements within pre-existing mineral aggregates. During the metasomatic granitization of hornblende schists to hornblende granodiorite, both uranium and thorium brought in by the granitizing fluids seem to have been preferentially incorporated in sphene, allanite and other accessory minerals; this caused rather erratic distribution of both these elements in the granitized series of rocks.

CONCLUSIONS

The data on the distribution of uranium and thorium as presented here are yet too meagre to hazard even a guess at the source of uranium mineralization along the Copper Belt thrust zone. As will be noted from Fig. 1, the specimens of Singhbhum granite whose uranium-thorium data are presented here lie over 30 km away from the outcrops of the Copper Belt thrust zone. Detailed studies on the uranium-thorium distribution in the Singhbhum granite near its northern borders, which are now under way, are expected to throw light on uranium mineralization along the thrust zone.

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